UNCLASSIFIED

AD NUMBER

AD488384

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 31 AUG 1965. Other requests shall be referred to Office of Naval Research, Arlington, VA.

AUTHORITY

ONR ltr, 18 Aug 1967

THIS PAGE IS UNCLASSIFIED

Monsanto Company/Washington University

ARPA Project

"High Performance Composites"

TAPES AND RIBBONS IN COMPOSITES:

A Literature Survey

Charlotte M. Bower, Editor

Richard A. Landy

John D. Calfee, Program Manager

Each transmittal of this document outside the Department of Defense must have prior approval of the Director, Material Sciences Division, Office of Naval Research

August 31, 1965

Monsanto Company/Washington University
St. Louis, Missouri

Joint program sponsored by the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-66-C-0045, order number 1001/58(C-65-006).

FOREWORD

The research reported herein was performed under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-66-C-0045, order number 1001/58(C-65-006).

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. John D. Calfee (Phone: 314-WY 3-1000, station 3754). The work is done by Washington University, St. Louis, Missouri with Dr. James M. McKelvey (Phone: 314-VO 3-0100, station 4464) as Project Director, and Monsanto Company, Central Research Department, St. Louis, Missouri, with Dr. John D. Calfee as Project Director.

The contract period is from 30 June 1965 to 30 April 1967. The amount of the contract is $2,000,000.

HPC 65-5

TAPES AND RIBBONS IN COMPOSITES:

A Literature Survey

Charlotte M. Bower, Editor

Richard A. Landy

John D. Calfee, Program Manager

Monsanto Company/Washington University
St. Louis, Missouri

August 31, 1965

Prepared for the Advanced Research Projects Agency under Contract N00014-66-C-0045, Order Number 1001/58(C-65-006)

ABSTRACT

Two-dimensional microstructures, e.g., flakes, plates, tapes and ribbons, offer unique properties as reinforcements for composite materials. There is little reported work in this area. The majority of the references are to glass, mica, and metal flakes which have been examined for electrical uses. Fabrication methods for glass flakes have received the most emphasis from industry. A few papers dealing with tapes and ribbons are cited.

TABLE OF CONTENTS

I. INTRODUCTION

This report treats the subject of tapes and ribbons in composite materials, or more commonly, the class of reinforcements for composites which are characterized by parallel faces. There has been extensive literature published in the last twenty-five years on fibrous and particulate reinforcing agents but very little work has been done in the field of two-dimensional reinforcements. Yet, this aspect warrants much consideration because of the special properties afforded by two-dimensional microstructures. Whereas, fibers afford unidirectional properties and particles afford hardness, flakes offer isotropy in the plane of the flake. The types of geometries of interest in this discussion are: first, tapes and ribbons, that is, flattened fibers connected to form a microplane; second, flakes or platelets of appropriate materials such as glass, mica, etc.; and finally, fibers of non-circular cross-section, especially elliptical fibers.

The type of approach used in the literature warrants a short explanation. There are two methods by which scientific phenomena may be explained, the analytical approach which attempts to describe the behavior of a composite on a microscopic or elemental scale, and the empirical or "black box" approach which compares the input and output of a composite system. Unfortunately, the more instructive and theoretical analytical approach is embraced by only a very small portion of the literature. Much of the material available on this subject lacks insight and basic understanding.

There also must be a few words devoted to the class of material found. Literature on tapes and ribbons is extremely scanty with fabrication methods mainly stressed. There is also a dearth of material on the third class, i.e., fibers of non-circular cross-section. Thus, nearly all of the references deal with flakes or platelets of glass, mica, and metal as the reinforcing agent.

II. DISCUSSION

Since there would be no reason for any research on flakes if they did not possess some special properties, it would be instructive to discuss six characteristic properties of flakes and flake composites.

First, two-dimensional microstructures offer a more desirable packing arrangement than fibers or particles. From a mathematical analyses, the closest packing design of fibers assuming ideal conditions, i.e., infinitely long fibers, would reach only a little more than 90% reinforcement by volume and, a similar argument, particles would achieve only 76%. But, since flakes are ideally flat planes, theoretically 100% reinforcement could be obtained. (See Figure 1) This better packing arrangement is beneficial for two reasons. First, one of the basic concepts behind composite materials is to impart the properties of the reinforcement to the system; a higher percentage of glass would result in higher strength, greater stiffness, and a higher strength to weight and modulus to weight ratio. Further, in general, the strength of binders increases markedly as the thickness of the binder layer decreases. Thus, the closer packing of flat surfaces against each other should produce greater strength in the binder layers. Therefore, the mechanical properties of the composite are enhanced in several ways due to a closer packing arrangement.

The graphs (Figures 3 and 4) show the effect of glass concentration upon tensile strength and flexural modulus. The curves are presented as bar curves due to the range of values obtained for laminates with the same flake glass content. At lower glass concentrations, the range of values obtained is decidedly narrower, presumably because laminate defects, such as air bubbles, and fine glass particles, have less of an effect in the low than in the high-glass content laminates. The physical properties of laminates below 55 weight percent and above 85 weight percent were not determined.

Closely associated with this type of packing arrangement is the very critical factor of parallel orientation of flakes in a composite. Non-parallel orientation of flakes would cause the composite properties to suffer considerably. For instance, a significant diminution in mechanical properties would result from the presence of high stress concentrations at the edges of the aslant flakes, leading to premature failure of the system.

Second, flake composites offer high resistance to liquid or vapor penetration. One of the major problems of fibrous and particulate systems arises from the weakening effect of water and water vapor penetration on the adhesive bond between matrix and reinforcement. But a composite with flakes in continuous, overlapping layers significantly reduces permeability for the following reason. Since the reinforcement is impenetratable, the agent is forced to pass through the composite via the tortuous matrix path (see Figure 2). This "tortuosity" factor would prevent damage to the matrix-

reinforcement bond and hence preserve the mechanical properties of the system. A reasonable amount of research has been undertaken in this area and some specific laminates, tested by Olin Mathieson, employing larger flakes and free from air bubbles and voids, were shown to be as impermeable by water vapor as aluminum foil.

An important application of the above principle lies in the field of corrosion resistance. A system of glass flakes suspended in a corrosive-resistant medium, such as a special formulation of bisphenol polyester resin, in a parallel, overlapping orientation has been established commercially as a new heavy duty corrosive-resistant coating. In addition, this multilayered system offers a high degree of toughness and resistance to abrasion and errosion, high resistance to thermal shock, and resistance to vapor transmission. Flake systems are presently regarded as superior to ground mica, calcium silicate, glass cloth, and glass mat systems in the field of materials protection.

Third, both electrically and thermally conductive and non-conductive laminates can be obtained with flake reinforcements. Extremely efficient conductors can be produced by arranging appropriate metal flakes, e.g. nickel or silver in a continuous, touching arrangement. On the other hand, reinforcement by non-conductive materials such as mica flake or glass flake, in a perfectly parallel and overlapping arrangement would afford very poor transmission of heat and electricity according to the principles outlined above.

Mica has always taken priority in the field of electrical insulation. In the rudimentary stages, natural mica flakes were used in insulating materials; however, these materials lacked desired mechanical properties, e.g., stiffness. In the past few years, a formulation known as mica paper has been produced which combines outstanding electrical properties with the desired mechanical properties. The mica flakes, either natural or synthetic, are placed in an oriented fashion in a suitable liquid suspension to provide strength and stiffness. Most of the present research is directed toward improving mica paper systems. Some research is also taking place on glass flake dielectric materials.

Metal flakes have been used extensively in electrically conductive systems. A composition of fiber flakes, graphite, and epoxy resin has been established as a conductive coating for electrical heating. A nickel-polystyrene composition has also proved to be a noteworthy conductor. As a final application, metal alloy flakes, such as nickel-iron alloys and iron-aluminum alloys, have been used in inductors. The advantages of using flakes are a higher magnetic permeability factor by eliminating air gaps, low eddy current losses, and a physically smaller core size.

Fourth, one of the obvious characteristics of flakes is that they are theoretically isotropic in the plane. This is true of ideal circular flakes and somewhat true for square and rectangular flakes. Hence, a planar flake has certain advantages over the unidirectional fiber. For example, if a uniaxial load is applied to a composite, only those fibers which are oriented

in that direction in the plane will assume the stress, whereas every flake in the plane will help to take up the applied stress. Thus, while fibers are strong in only one direction, flakes are strong in all directions; and the properties of fibers drop off rapidly at angles away from the fiber axis. Hence, flakes offer a more favorable strength to weight ratio in the composite plane than fibers. Since this ratio is an important design criterion for structural applications, much research has been undertaken in this area. Much of the attention has been directed to the field of stress concentrations and improvement of tensile properties. Some work has also been done on fabrication of cylinders and shapes other than flat plates by fluid molding pressure.

Fifth, flakes theoretically offer superior strength properties. Special consideration must be given to moduli of elasticity. Flakes offer much higher moduli of elasticity than fibers because flakes have fewer degrees of freedom. If the bending possibilities of each microstructure are explored, it is easily seen that a fiber can be bent sideways as well as around the center of bending whereas flakes can be bent only around the center of bending; therefore, fibers would accommodate new positions more readily than flakes. This accounts for the lower fiber moduli. Theoretically, the various strengths of flakes should also be great but this has been verified only in the case of compressive strength. Reasonable values have been obtained in flexural tests but still not as high as predicted. Very low tensile strength has been one of the major faults of flakes; the most critical factor is the surface conditions of the flakes. Much of the present research deals with the improvement of tensile properties. M. A. Sadowsky has shown in an analytical paper that planar flake arrangement would be essentially worthless because stress concentration would be very high at the end of the plane. However, he proved mathematically that a staggered flake arrangement would permit force transfer by shear stress and thus fully exploit the strength properties.

Experiments have shown that mechanical properties of flake composites are dependent to a large extent on flake thickness. For example, qualitative plots (see Figure 5) of flexural strength and modulus against flake thickness indicate that these properties suffer rapidly with increasing thickness in a nearly linear fashion. Other problems can arise, however, if the flakes are too thin, e.g., handling difficulties. Thus a compromise must be reached between these considerations. Somewhere in the neighborhood of 5-8μ thickness seems to be generally accepted. On the same line, experiments have also indicated that there is an optimum diameter to thickness ratio. A high ratio, i.e., large flakes, presents the problem of physical difficulty of mixing. Large and small flakes together yield bridged structures conducive to air voids, etc., leading to signficant damage to the composite characteristics. Again a compromise is necessary to choose a "medium" flake which would arrest any major problems and still offer good mechanical properties. A further design consideration is minimum thickness of resin binder for reasons stated previously. As is indicated in the graph (see Figure 6) failure will occur through the matrix if the matrix thickness is not kept very low. A final requirement for high performance flake composites

is that they must be completely free from bubbles, voids, etc. This factor is more critical in flake composites than in fibrous or particulate systems because trapped bubbles and air pockets are extremely difficult to remove, since in a flake reinforced structure bubbles cannot rise without being pushed sideways. Any pressure exerted might flatten and split the bubble causing local dewetting and failure through delamination.

Therefore, it is apparent that the "ideal" flake composite would consist of a very large number of very thin flakes in parallel orientation bonded by very thin adhesive layers and free from defects. The arrangements of the falkes would be such that each flake overlapped and was bonded to all the flakes contiguous to it.

Optical properties of flat plates have opened up a new field of technology to flake composites, the field of reflective coatings. A system of aluminum flakes suspended in a coating resin such as cellulose, vinyl, or acrylic resins, is used as a roof coating because of its high heat reflectance and impermeability characteristics. Aluminum pigments are used to produce a silky appearance like mother-of-pearl when the flakes are oriented to reflect light in designated directions. Various decorative effects can be achieved by different combinations or arrangements of the metal flakes. Recent developments have led to research on metals, such as copper which possess heat stability and is anti-corrosive, silver, and gold; also alloys such as copper-zinc alloys are being explored. The major problem in the field of metal flakes is the lack of adequate yet inexpensive fabrication techniques. One of the more promising metal flake production methods is the thermal decomposition of organometallic compounds in the presence of smooth discrete glass flakes, where the metal is of the chromium, aluminum, molybdenum, or nickel family.

Just as inserting reinforcements in a matrix proved to be a profitable idea, so a good deal of research has recently started on mixed reinforcements to utilize the characteristic properties of each type of agent. Of special interest, is flake-fiber reinforcement. The results of strength tests have indicated that in one particular instance the flexural strength of glass flake increased by 135% and glass fiber by 17.9% in such a composite, while the compressive strength of the glass flake increased by 48.9% and the glass fiber by 32.7%. Unfortunately, in the very critical area of tensile strength, no data of this kind is presently available. It is anticipated that the high moduli and impermeability properties of the flake and the low density and directional properties of the fiber can be fully exploited in this type of combination. It seems to the author that a possible theory supporting the experimental results concerning these strength increases is based on the stabilization effect on the glass fibers by the glass flakes. This is easy to visualize because fibers are of such a columnar shape that they would fail in buckling before yielding in flexure or compression. Hence their dimensional arrangement leads to instability before yielding; if this instability could be avoided by some stabilizing effect so that the fibers could not deflect very far out of the stress plane, a much stronger composite would result One method of achieving stability is by placing flakes, which have high compressive strength, on top of the fiber planes to restrict the bending of the fibers.

The potential of flake-fiber composites for engineering applications is excellent because the mixture of the two reinforcements yields low density, low impermeability, respectable strengths, and high moduli of elasticity. In fact, there are already a couple of applications: a filament wound battery case which requires impermeability to electrolytic solutions and good biaxial strength and underwater vessels which require excellent compressive strength and water impermeability.

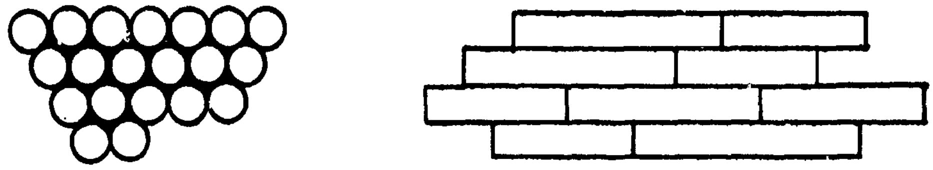

FIGURE 1

Packing of Circular and Rectangular Cross Sections

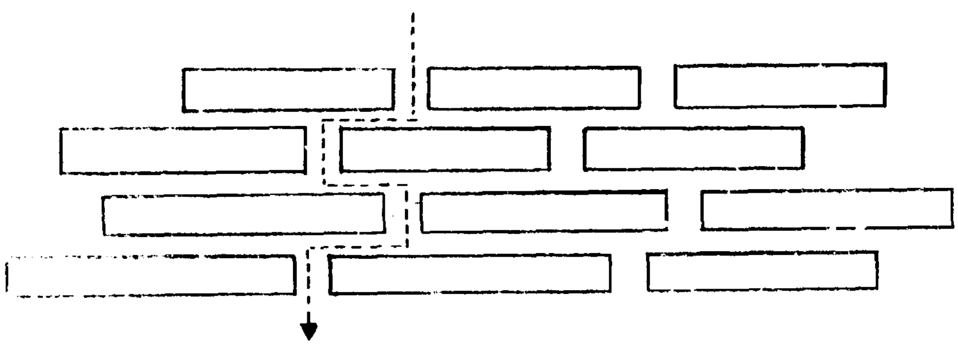

FIGURE 2

Path of Molecules Penetrating Flake Laminate

(... Gilman: "Properties of Glass-Flake Reinforced Plastics" ...santo Company Boston, Mass. p. 309 AD 233 158, Proc. ...th Sagamore Ordnance Materials Research Conference.)

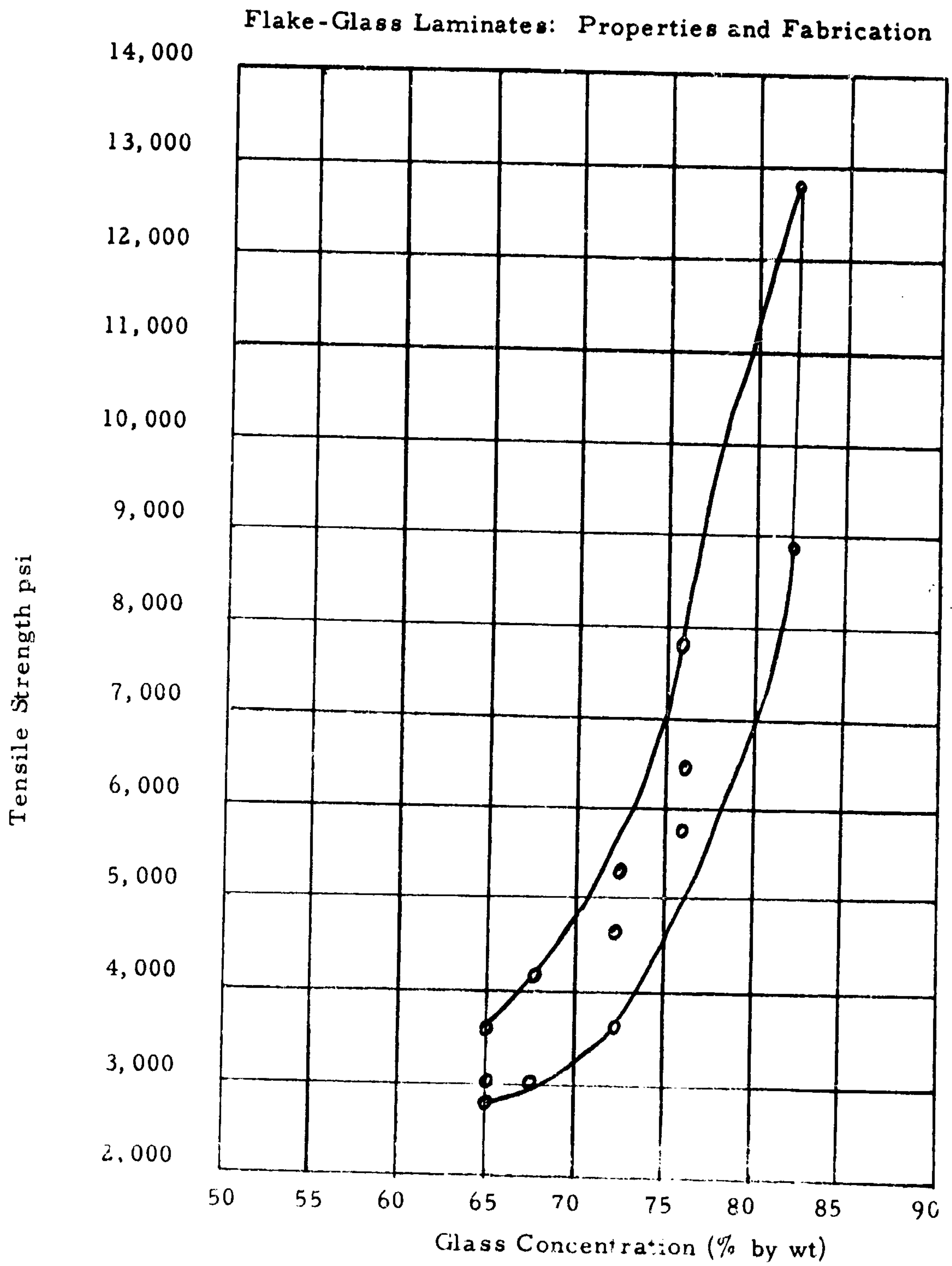

Figure 3: Effect of Glass-Flake Content Upon Tensile Strength

(Plastec Report 1, State of the Art: Flake-Glass Laminates, AD 244 104 October 1960, Picatinny Arsenal, p. 83.)

Flake-Glass Laminates

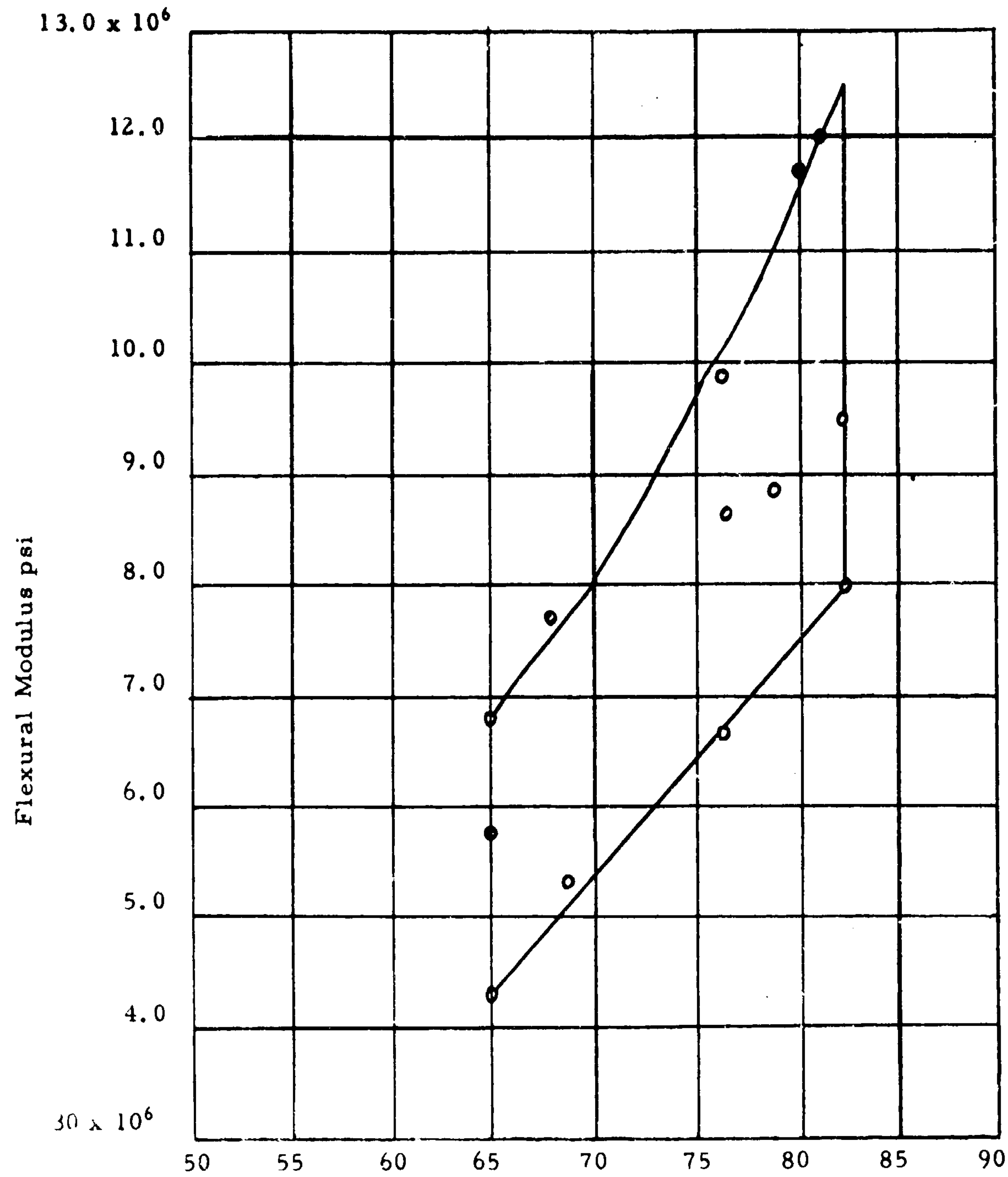

Figure 4: Effect of Glass Flake Content Upon Flexural Modulus

(Plastec Report 1 State of the Art. Flake-Glass Laminates AD 244 104 ...., 1960, Picatinny Arsenal, p. 82.)

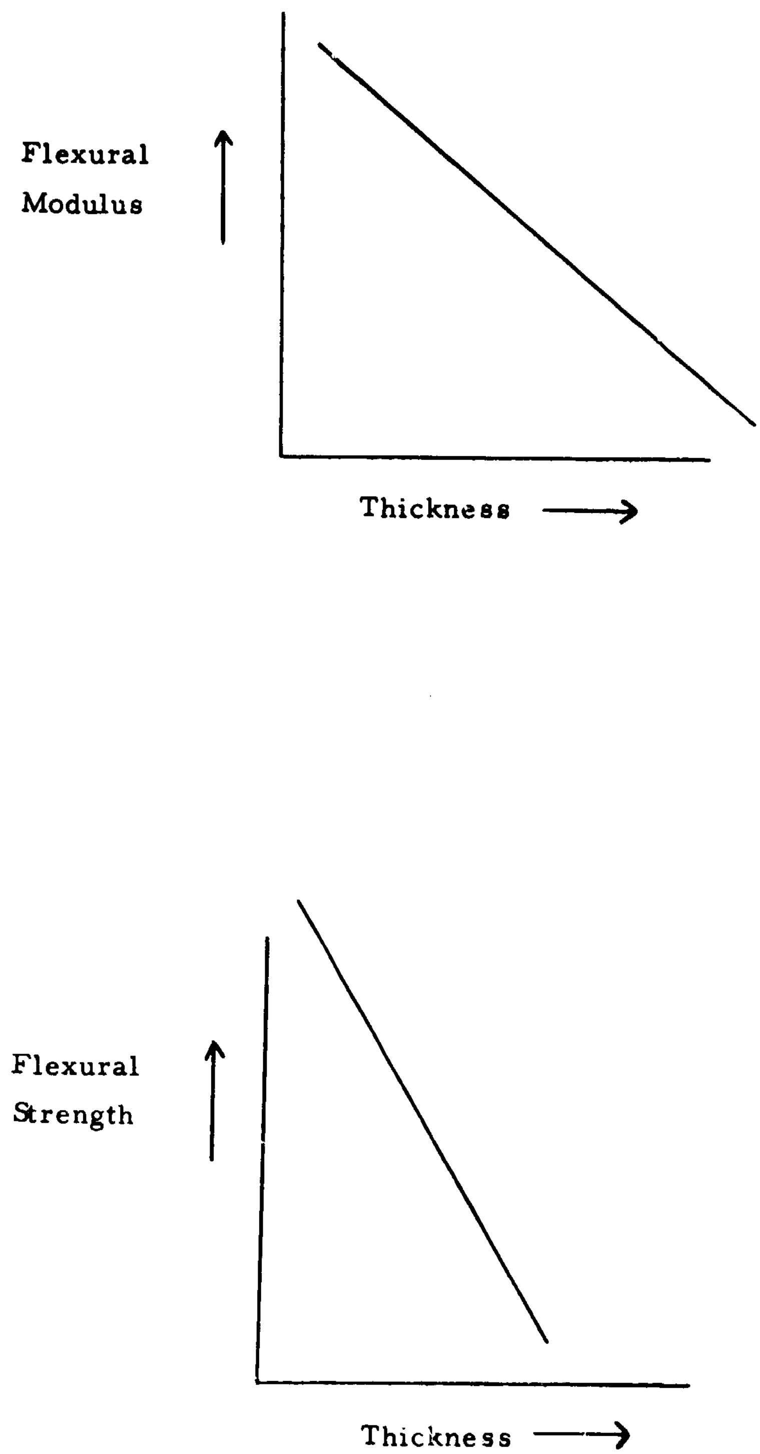

FIGURE 5

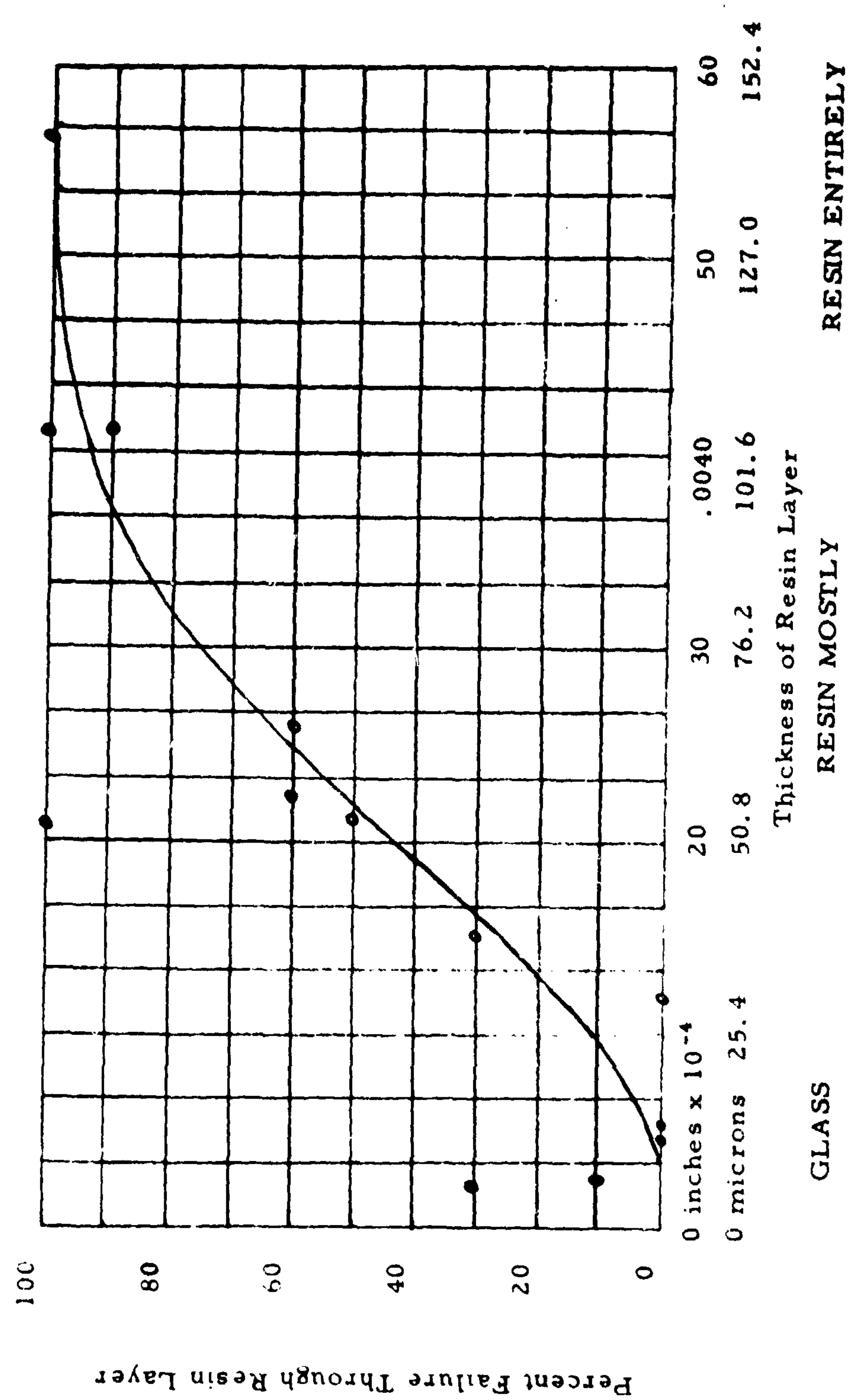

Figure 6: Percentage of Failure Through Resin vs Thickness of Resin

(The Promise of Composites: <u>Materials in Design Engineering</u>, No. 210 9/63, p. 97.)

III. CONCLUSION

In summary, the technology of mica flake and metal flake is fairly advanced. The state-of-the-art of glass flake is still rudimentary. Not an extensive amount of research has been devoted to two-dimensional reinforcements in general. Tapes and ribbons have been almost entirely untouched; but this field offers great possibilities as a method of combining the directional fiber properties and the omnidirectional flake properties in one reinforcement. In the field of glass flake, one cannot categorically state superiority in any consideration or characteristic, because there are other composites superior to glass flake composites in any tested performance. The prediction of low cost factor is precarious because of the many imponderables influencing price structure. Also, a chopped fabric compares faborably in both properties and economic factors. The essence of the question is not how much better or cheaper flake composites are than fiber systems, but rather what functions can flake composites perform better than present systems. The salient problems which must be overcome before flake composites can establish themselves as high performance materials are imprcvement of the flake surface condition and tensile properties and testing of flakes under large-scale production techniques. Applications of flake composites have been limited and hence there is no definite indication of their performance. But, it is the general consensus that much more research is warranted in the field of two-dimensional reinforcements.

IV. BIBLIOGRAPHY WITH ABSTRACTS

A. GLASS FLAKE

1. Applications

(a) Electrical

Adams, E. and Hubbard, W. M. (U. S. Dept. of Navy), "Insulated flake-type magnetic cores," U. S. 2,937,964, 5/24/60.

Magnetic cores are built up of insulated, oriented flakes of Ni-Fe alloys. The alloy is rolled to a fine-equinaxed grain structure which is fractured and crushed mechanically. The flakes are formed by cold-rolling the resulting powder. They are insulated with a talc or kaolin-$Mg(OH)_2$-Na_2SiO_3 mixture aligned, compacted at 100 T/sq. in. annealed, and rapidly air-cooled.

Previous cores have been known for their low permeability factors due to air gaps. The layered flake particles are such that there are fewer air gaps and hence a higher μQ factor for the core. The new cores is also characterized by low eddy current losses, and by a physically smaller core size.

Adams, E, Syeles, A. M. and Hubbard, W. M., "Magnetic cores composed of iron-aluminum alloy flakes," U. S. 2,864,734, 12/16/58.

Magnetic cores having high permeability, low power loss, and free of Ni or Mo are composed of Alfenol containing 10-17% Al with the rest chiefly iron, ground to 30-60 mesh particles which are subsequently flattened to flake form by rolling at about 200°. The flakes are then coated for insulation with a metallic (Al_2O_3) oxide. A metallic binder is used to compact the flakes to form the core. The inventor describes the method by which each of the above steps is carried out.

Thurnheer, H. (Fabrik elektrischer Apparate Sprecher and Schuh AHT.-Ges.) "Electrically insulating plastic material." Swiss 330,282, 7/15/58.

Plastic insulators are less moisture resistant than ceramic ones. However, their moisture resistance is improved by incorporation of glass scales or mica platelets and orienting them so that they overlap to form a virtually moisture impermeable barrier.

Williams, W. D. (to Sperry Rand Corp.). "Binders for conductive metallic films," U. S. 2,880,181, 3/31/59.

Metallic flakes of conductive materials such as Ag, Cu, Al, or Au-Ag alloys, using nitrocellulose in EtOH and EtOAc and cellulose acetate butyrate in MeCOEt and toluene (with dioctyl phthalate as a plasticizer) as binders, are applied to shaped plastic structures to form coatings conductive to microwaves. The products are useful as waveguides.

(b) Corrosive

"Flake-glass coating resists corrosion," Materials in Design Engineering, Vol. 57, No. 5, p. 95, May 1963.

Glass-flakes suspended in a special bisphenol polyester resin protects metal surfaces from corrosion, electrolytic attack, erosion and abrasion.

The peculiar properties of Flake-glass Coating M-103 (trade name) are its impermeability to liquids, resistance to thermal shock and cracking because of its coefficient of thermal expansion, great adhesion, and reduction of stresses during curing. Application in heavy thickness provides toughness and resistance to abrasion under erosion conditions.

The method of application by airless spraying is discussed in a little detail and a few successful applications are noted.

Einhorn, I. N. and Crecca, J. D. (Owens-Corning Fiberglas), "Accelerated tests show glass-flake filler improves the performance of polyester resin coating," Materials Protection, 2(7), 10-12, 14, 17-18 (1963).

Coatings consisting of a modified bisphenol polyester resin filled with glass flakes were significantly better in accelerated tests in liquid and gaseous phase solutions of hydrochloric acid, acetic acid, and phosphonic acid and distilled aerated water at 160°F. Comparison was made with other coatings using the same vehicle, filled with ground mica and calcium silicate. Glass-flake coating also out-performed glass-cloth laminates and glass-mat cloth in both sodium hydroxide and acetic acid at 180°F. Better performance of glass flake filled coatings was noted also in tests for vapor transmission rates, salt spray exposures thermal shock, temperature-humidity cycling, accelerated weathering, and abrasion.

"Glass flakes: key to new strong coating," Chemical Engineering, Vol. 67, No. 18, p. 162 164 166 9/5/60.

Development in corrosion protection, "reinforced" spray coating containing glass flakes coating produces hard thick barrier consisting of multiple layers of glass (for strength) interleaved in polyester resin (for chemical resistance): unusual feature is combination of glass flakes and resin in sprayable coating, material is manufactured from borosilicate glass specifically compounded for acid resistance, ultraviolet capacity and weatherability.

(c) Structural

"Establishment of the potential of flake reinforced laminates as engineering structural materials," AD 274 332, (1962).

The fundamental structural properties investigated during the first year of the program were advanced in detail and advantageous applications of flake composites were determined. Combinations of flake with glass fibers were tested and their structural potential is discussed.

The theoretical work conducted during the period covered by this report predicts inherent stress concentrations of up to eight times the nominal stress in circular flake compositions.

The fabrication of cylinders and shapes other than flat plates using preformed, b-staged sheets of flake composite material and fluid molding pressure is reported to have advantages over other fabrication methods.

"Establishment of the potential of flake reinforced composites as engineering structural materials," <u>AD 265 192</u>, (1961).

An analysis of the moment distribution on a uniformly loaded circular plate with edges overhanging the support is presented. The equations developed are used to calculate the maximum tensile stress and deflection in such a loaded plate. These equations are intended for the evaluation of the flexural strength of flake reinforced plastic laminates under biaxial stress.

The notched tensile strength of flake laminates is reported. The results are interpreted in terms of built-in stress raisers caused by local variations in the distribution of flake. Tensile strength at root of the notch has reached a level of 5.8×10^4 psi.

"Establishment of the potential of flake reinforced composites as engineering structural materials," <u>AD 266 379</u>, (1961).

Composite material studies indicated that combination of flake and fiber in a laminate will provide high compression, flexural, and tensile strengths.

Additional studies provided data to substantiate the theory that flake laminates are insensitive to stress concentration.

Techniques were evaluated for molding cylinders of glass flake material. Limited success was achieved which indicates that quality cylindrical flake laminates are possible.

Studies on thread shear strength and machinability indicate that flake laminates could be used efficiently for inserts in primary structures.

"Establishment of potential of flake reinforced composites on engineering structural materials," <u>AD 265 263</u>, (1961).

An evaluation of geometric concentration effects of circular lap joints was conducted. This included the development of methods of analyzing circular lap joints, and experimental verification of concentration factors at edge of flake up to 4.

The notch sensitivity of flake reinforced composites was evaluated. Although flake reinforced composites behave as brittle materials, they were determined to be relatively insensitive to notches, experimentally.

The electrical properties of glass flake reinforced composites and mica flake reinforced composites were evaluated and compared. Mica flake composites appear to be as good as glass flake composites.

A preliminary mechanical investigation of mica flake reinforced composites was made, indicating that mica flake has definite advantages, particularly with respect to increasing the stiffness of the composite. Flexural modulus of 10^7 psi was attained in a mica flake composite.

"Establishment of the potential of flake reinforced composites as engineering structural materials," AD 240 725, (1960).

A statistical analysis of the variation of flake distribution within a flake reinforced composite has been performed and verified by an experimental evaluation of cross sections taken at random throughout the composite. No correlation has been found between the variance in flake proportion in a cross section and the variance in mechanical test data. The thermal stress developed in a glass-resin composite, due to large difference in thermal expansion between components, has been examined photoelastically. Thermally induced shear as large as 400 psi has been observed. Model laminates from circular flakes have been tested in tension to check a prediction of composite strength as deduced theoretically. Preliminary results indicate good agreement between theoretical and observed values. A strength-to-weight analysis for plates and cylindrical elements in compression has demonstrated the superiority of present day glass flake laminates over aluminum and steel for application where the principal mode of loading is compression.

Included in this report is a discussion of metal flake composites.

"Establishment of the potential of flake reinforced composites as engineering structural materials," AD 239 751, (1960).

A theoretical analysis of behavior under stress of circular glass flake reinforcing elements in a resin matrix is presented. The ultimate compressive strength is a function of specimen and flake thickness. Lower limit values of ultimate strength have been estimated from reasonable glass and resin properties. Methods for determining mechanical properties are given. A calculation of the stress induced in a flake composite from thermal effects has been made. The thermal stress is a function of localized structure within the composite and can be extremely high.

A method of testing tensile strength of individual circular glass flake has been developed and verified. The average tensile strength of the flakes tested falls in the range of 1.5-2.0 x 10^5 psi, the flake formed from Pyrex glass can be made as thin as 0.5 mils with a d/t ratio of 250. Theoretical calculations based on reasonable glass and resin properties indicate a minimum d/t ratio of 220. A statistical criterion for the selection of a non-arbitrary flake slenderness ratio is suggested.

"Establishment of the potential of flake reinforced composites as engineering structural materials," AD 265 929 (1960).

The stress-strain behavior of highly idealized model flake composites, composed of disc shaped flake of uniform size and mechanical properties.

has been considered. An analysis of such a composite under a uniaxial tensile stress has been performed, considering the reinforcing elements to act independent of their nearest neighbors. This analysis was modified to consider interactions between adjacent flakes. For independent case, upper strength limit is 48% of inherent strength of reinforcement, independent of d/t ratio once a minimum is reached and independent of packing, as long as it is parallel. For interaction case, a larger fraction of reinforcement can be developed by fixing the d/t ratio and flake arrangement.

Techniques for making disc shaped glass flake are given, and results listed. The lenticular form is also discussed for hopeful increase in efficiency.

The mechanical properties of present day glass flake laminates are given and a weight-strength comparison to Al and steel is made. Based on weight-strength criteria, it is shown that glass flake laminates are superior to both the aforementioned materials for various configurations under compression.

"Establishment of the potential of flake reinforced composites as engineering structural materials," AD 270 502, (1962).

Increase in strength over flake alone, or fiber alone, for flake-fiber combinations are reviewed. Techniques for centrifugally casting flake cylinders are reported. A continuation on studies of notch sensitivity of flake composites still shows their relative insensitivity to concentrators. Data on mica flake-glass fiber combinations are presented.

Very significant increases in the modulus of flake composites with a carbon black filler are discussed, along with some applications of flake.

Pehrson, A. G., "Designing with glass bands," SPE Journal, Vol. 18, No. 3 301-306, (March 1962).

Pre-stressed resin impregnated unidirectional glass tapes are explored in this article for use in rotating electrical equipment. The type of material discussed is that in which glass fibers are continuous and grouped together in bundles held by a resin, the most common being a polyester. The role of the resin is to distribute stresses equally to all of the glass ends.

The body of the article is devoted mainly to a stress analysis in the light of its use in electrical equipment with no real specific conclusions drawn.

(d) Optical

Schroeder, H. and Kauffmann, R. (Jenaer Glaswerk Schott and Gen), "Perlaceous fibers," G.P. 1 136,042, (Sept. 1962). (Appl. Nov. 1959.)

Filler materials having artificial mother-of-pearl gloss consist of flakes or lamellas of oxides or oxide hydrates of metals of Group IV or V or the Fe Group, the thickness of the flakes being about 1/10 to some

multiples of the light wavelength. The flakes consist of alternating layers of partial flakes of lower and higher n respectively. The flakes of higher n consist of oxides of Ti, Fe, Sb, Sn, Th, Zr, those of lower n substantially of SiO_2. The flakes are embedded in plastic or pasty binders, e.g., synthetic resins. The flakes are made by applying to a carrier a solution of a compound of the metals, drying the layer with simultaneous conversion thereof in an oxide or oxide hydrate film, and splintering the film in the form of the desired flakes.

(e) Other

Callinan, T. D. and Lucas, R. T., "Properties of paper made from glass flakes," J. Electro-Chem. Soc., 103, 543-5 (1956).

The preparation and properties of paper made from glass flakes are described. The electrical properties of a capacitor made from this paper are presented. Glass-flake paper was impregnated with varnishes and became mechanically strong and water resistant.

Tables are given for the properties of 100% glass-flake paper and properties of varnish impregnated glass flake paper.

Owens-Corning Fiberglas Corp., "Films reinforced with siliceous flakes," Belg. 618,327, (Sept. 1962). (Appl. May 1962.)

Thin, rigid, polymeric films, having low water-vapor permeability and high electrical resistance, are formed by coating flakes of glass or mica with a monomer of unsaturated hydrocarbon, which is polymerized in situ, and forming the resulting flakes into a continuous film. Thus, flakes of glass, 1-6 mμ thick and >25.4 mm, or flakes of mica, suspended in toluene, are treated with $TiCl_4$ and N at 140°, until 1 part $TiCl_4$ is absorbed by 30 parts of glass. After purging with N, a mixture of 0.05 moles of iso-Bu_3Al in 1200 ml toluene is added, and C_2H_4 gas is introduced at 60°. The treated flakes are cooled, washed, filtered, and dried, and passed between rolls at 163° to obtain a film of 0.076 mm thickness.

Phillip, H. J. and Phillip, I. (VEB Lokomotivbau-Elechtrotechnische Werke), "Insulating glass paper," G.P. 1,123,720. (Feb. 1962). (Appl. Sept. 1958)

Glass flakes are suspended in H_2O, and the glass paper is made from this glass-flake pulp in a paper machine without use of binders. Optionally, inorganic fibers, e.g., glass fibers, or cellulose fibers may be added to the glass flakes.

Shannon, R. F. (Owens-Corning Fiberglas Corp.), "Reinforced metallic-salt materials," Belg. 629,076, (July 1963). (U.S. Appl. Jan. 1963.)

The reinforcing materials are glass fibers or flakes. Materials so constituted are indicated as gaskets for high-temperature joints; the plasticity is supplied by the salts in a microcrystalline state and rigidity by the reinforcement. A nonlimited list of 33 appropriate salts is given. Various examples are included.

Slayter, G. (to Owens-Corning Fiberglas Corp.), "Glass-reinforced articles," <u>U.S. 3,080,247</u>, (Mar. 1963). (Appl. July 1957.)

Articles such as rods and gaskets of AgCl or TlCl, reinforced by flakes or fibers of glass, are prepared by melting the metal halide and pouring it into molds filled with the glass reinforcement in the desired proportion. The percentage of glass must be at least 5% and can be ≥ 50%. Rods tested for flexural strength showed 42,000 lb./sq.in. Gaskets made of the metal halide and fiber glass can slowly deform without breaking.

Slayter, G. and Shannon, R. F. (to Owens-Corning Fiberglas Corp.), "Glass-reinforced gypsum composition," <u>U.S. 2,970,127</u>, (Jan. 1961). (Appl. Dec. 1954.)

The plaster mass consists of gypsum, a synthetic resin (melamine-HCHO, phenol-HCHO, or urea-HCHO) and 50-70% by weight of flakes of glass. The glass flakes lie parallel to one another, thereby providing greater resistance to passage of vapor, moisture, and electric charges through the mass. Glass fibers have proved unsatisfactory because of low weight incorporation.

2. Fabrication

(a) Emhart Manufacturing

"Investigation of flake laminate," <u>AD 52 970</u>, (Sept-Nov. 1954).

Preliminary experiments on the formation of flakes by feeding hot beads from a "Schori Pistol" between rotating rolls were performed. Few of the flakes formed were free from edge cracks. However, the results obtained are considered to be of sufficient interest to warrant further experiments in the same direction with improved equipment.

"Investigation of flake laminate," <u>AD 58 323</u>, (Dec-Feb. 1955).

Attempts to roll glass beads of various sizes into flair free flakes led to the conclusion that the beads were not hot enough during rolling process. These experiments were performed with the beads fed into rolls by air entrainment through a flame. To provide more heat to the beads during rolling, the equipment was rebuilt to allow gravity feed of the beads through a chamber heated by radiation which would simultaneously heat the rolls.

In order to determine the feasibility of blowing an unsupported sheet into flakes before investing in platinum equipment, experiments were conducted on Cellolyt 102 instead of glass. The material was extruded as a ribbon between opposed air jets in the hope that biaxial stretching would produce flakes. Although mostly fibers were produced, a few flakes with irregular edges resulted.

"Investigation of flake laminate," AD 60 450 (March 1955).

Preheated borax and glass beads were dropped into heated rolls in preliminary experiments. No conclusions could be drawn as the rolls were kept from closing properly by material which stuck to them.

Difficulties were also encountered with convection currents blowing up through the preheated oven.

Experiments with air jets blowing against an extruded ribbon of Cellolyn 102 produced some curved flake apparently of micron thickness. The results were of sufficient interest that further work will be done varying air jet geometry.

"Investigation of flake laminate," AD 67 476, (March-May 1955).

Attempts to produce flakes or tape by flattening heated beads and tubing between rotating metallic rolls have been continued.

The flattening of beads and fiber to small thicknesses (under .001) by means of rolls at 500°F did not yield any promising samples because of excessive cooling by the rolls. Experiments with rolls heated at the nip above 500°F were not conclusive, because of insufficient control of roll surface temperature.

Experiments have been started on pulling tape from a platinum lip on the edge of a pot of molten glass. The best result of preliminary trials was a glass tape 0.020 inch wide by 0.002 inch thick with a bending strength of about 200,000 psi.

"Investigation of flake laminate," AD 70 385, (July 1955).

Preliminary investigation was made of a film stretching method which employed two wires that traveled through the material to be stretched, out a slot, and then diverged. The method applied to molten shellac resulted in film 0.0003" thick.

A special transformer which could be used with the proposed platinum melting unit was found available commercially.

"Investigation of flake laminate," AD 90 077. (Jan. 1956).

Work is almost complete on the assembly of a new furnace to preheat diverging wires.

Design and procurement have proceeded on apparatus to try stretching glass film between diverging peripheries of two wheels.

"Investigation of flake laminate," AD 73 626, (June-Aug. 1955).

An order was placed for a platinum melting unit containing a slot from which glass tape may be drawn. The dimensions of the slot were suggested by the results of drawing melted shellac from slots of various sizes at variety of speeds and viscosities.

Shellac film 0.0003" thick resulted from a test of a film stretching method using two wires that traveled through the melted material, out a slot, and then diverged. Design and fabrication is proceeding on equipment suitable for applying this method to glass.

"Investigation of flake laminate," AD 81 931, (Oct-Nov. 1955)

An experiment was performed with equipment designed to stretch film with wires that descend through molten glass and diverge from an orifice below. Several improvements were indicated before satisfactory results can be expected:

1. Additional means to preheat wire.
2. A better means of maintaining tension in the wire.
3. Better control at slow wire velocities.
4. Higher temperature in the glass.

"Investigation of flake laminate," AD 98 626, (May 1956).

A preliminary attempt was made to stretch glass film between two rims revolving edge to edge. A region of film occurred, but separated into fibers before cooling. A more uniform rate of supply of glass and lower temperatures in a region of the film are indicated.

A summary of the work of the past year (July 1955 - May 1956) is included in this report.

"Investigation of flake laminate," AD 111 887, (July-Sept. 1956).

Experiments were completed with stretching rims set side by side on parallel axes.

The best samples of film produced were .0001" thick and about one square inch in area, but were curled by the cutting saws due to insufficient cooling. Steady conditions could not be achieved because the melting unit would not provide flow for long enough. Therefore, design and fabrication has been started on a new apparatus suitable for use under a much larger melting unit and incorporating stretching rims with axes inclined to each other.

"Investigation of flake laminate," AD 107 972, (Aug. 1956).

Increasing the rim temperature to 1900°F and decreasing the number of bubbles in the glass supply resulted in film as thin as 0.0001 inch thick. The best samples produced were clear and unstriated, but were curled by the cutting saws. Fibers were produced when the rims did not receive a sufficient supply of glass, and when exhaust interferred with film cooling.

Steady conditions could not be achieved because the melting unit would not provide uniform flow for long enough. Therefore, it is planned to rebuild the apparatus for use under a much larger melting unit.

"Investigation of flake laminate," AD 119 970, (Oct. - Dec. 1956).

This quarter has been devoted to design and fabrication of a new glass film stretching apparatus incorporating stretching rims with axes inclined to each other.

"Investigation of flake laminate," AD 134 894, (May 1957).

Conditions for stretching film with the inclined axes were determined and some film was produced.

In the light of new information regarding optimum rim speed, the melter used to date as an intermittent source of glass appears impractical to adapt to continuous feeding of the rims at a proper rate.

Alternate methods of feeding the rims are being investigated.

"Investigation of flake laminate," AD 139 073, (July 1957).

Determination of conditions for stretching film with present apparatus indicates the need for a method of feeding the rims at a much lower rate of flow than that obtainable from the present melter.

A new method of feeding, being investigated, involves winding a cold fiber of low-melting glass onto one of the rims.

"Investigation of flake laminate," AD 140 247, (July 1957).

This month has been devoted to planning and building apparatus to feed a rod of glass into an electrically heated tube. One of the stretching rims will pull a fiber from the heated rod; the fiber will then be stretched into film.

"Investigation of flake laminate," AD 143 910, (Aug. 1957).

Feeding a rod of glass into an electrically heated tube appears satisfactory as a means of supplying a fiber to the stretching rims. However, several changes in the equipment appear necessary before flake can be produced continuously. The most important of these relate to concentricity of the rims and the configuration of the edges.

"Investigation of flake laminate," AD 145 982, (Oct. 1957).

A satisfactory means of feeding the correct (0.3 oz/min) quantity of glass to the stretching rims has been developed. However, the rim mounting assemblies and the rims themselves have been redesigned in an effort to correct intermittent contact between them which resulted from eccentricity of the rims on their mountings.

"Investigation of flake laminate," AD 202 831, (Aug. 1954 - Jan. 1958).

Methods for flake production included: rolling glass beads, rolling glass tape, blowing extruded ribbon, drawing tape from a lip, drawing tape from a slot, stretching film by diverging wires, stretching glass film by rims having parallel axes, and by rims having inclined axes. The inclined axes was the most successful of all.

The conclusions drawn were: (1) the diverging rims can operate over a wide range of temperature and speed, (2) glass must be free of imperfections, (3) remnants of stretching should be remelted rapidly, (4) glass log.viscosity at 3.4 to 5.6, (5) production of continuous ribbon film is a definite possibility.

The improvements suggested for the inclined axes technique were: (1) continuous flow necessary, (2) more wettable rim material necessary and larger diameter for cooling etc., (3) rim position changed to provide means of collecting film and rim angle changed to allow for more cooling, (4) improved method of heating rims.

(b) Olin-Mathieson

"Development of manufacturing methods for glass flake reinforced plastics," AD 252 858, (Oct.-Dec. 1960).

This study is concerned with the development of manufacturing methods suitable for production of glass flake reinforced plastics by investigation of the applicability of epoxy, polyester, silicone, and phenolic thermosetting resin systems to the operations of compression molding, transfer molding, extrusion molding, centrifugal casting and calendering. Compression molded and calendered dry blend epoxy glass flake components have been produced. Calendering shows promise as a method for producing continuous sheet. Further development is required. Compression molded laminates produced by a centrifuge process yielded low strength laminates. Cast resin formulations have been prepared for use with glass flake formulations; i.e., epoxy, polyester, silicone, and phenolic systems.

"Development of manufacturing methods for glass flake reinforced plastics," AD 274 531, (Dec. 1961-Mar. 1962).

Investigation of the suitability of glass flake reinforced resin systems in commercial molding operations was completed upon the successful molding of rocket exhaust nozzles. Centrifugal cast pipes have been prepared from polyester and epoxy resin glass flake systems. The cast pipes have been produced with variations in inside and outside diameters and with metal inserts molded in the compression molded thickness studies of dry blended phenolic resin and Abbe-blended silicone resin systems have been completed. Wet glass flake blends have been processed by calendering. Sheets of several thicknesses have been molded and orientation of the sheets was excellent. Complex shapes have also been molded from dielectrically heated "B-staged" premixes which were oriented by the sheet forming process.

"Development of manufacturing methods for glass flake reinforced plastics." AD 274 531, (March 1962).

Investigation of the suitability of glass flake reinforced resin systems in commercial molding operations has been completed with the successful molding of the seventh configuration. The seven units molded are missile stabilizer functions, practice nose cones, ablative test nose cones,

windshield inserts, rocket exhaust cones, electronic gate assemblies and electronic frames.

Centrifugal cast pipes have been prepared from both polyester and epoxy resin-glass flake system with variations in both diameters and metal inserts molded in. Investigations are being conducted to devise processes for more complex shapes. Investigations are also conducted on dry blended phenolic resin systems.

Abbe-blended wet premixed epoxy glass flake systems have been processed into thin oriented sheets by use of the three roll-calender apparatus. A study to determine the effect of the process technique upon glass flake size and physical properties of the molded laminate is underway. The laminates are translucent, highly oriented, exhibit little pearloxalescence, and virtually free from visual defects. Complex shapes have been compression molded using dielectrically treated "B-staged" calendered sheets without reducing flake orientation and apparent quality of laminate.

"Prototype production processes for glass flake resin premixes and fabrication of parts by compression molding, transfer molding, calendering and centrifugal casting," AD 299 349.

Prototype production processes have been demonstrated feasible for preparation of glass flake resin premixes and subsequent fabrication of parts by compression molding, transfer molding, calendering, and centrifugal casting. Laminates have exhibited physical properties superior to previous reported systems. Dry blends and wet blends yield laminates with excellent appearance, voidless, free of bubbles etc. Complex shapes can be formed from dry and wet blends by compression molding. Studies were made on influence of various resin systems and flake size breakdown during processing.

Premix preparation was based on Abbe-blender for wet mixes and a Patterson-Kelley V blender for dry mixes. Other infeasible techniques investigated were plenum chamber coating, solvent coating, and centrifugal blending.

Resin classes investigated were epoxies polyesters, pherolics and silicones. Epoxy and polyester systems are readily mixed and processed in complex shapes and the former has superior strength and usual characteristics to the latter. Phenolic and silicones produced poor appearing or uncured moldings. Uses are listed.

(c) Owens-Corning

"Development of fibermix extrudable insulation," AD 264 768. (Apr. 1960).

The contribution of the woven glass braid layer in wires such as MIL-W-5086A wire has been found to be positive physical spacing from ground or from adjacent wire when the primary insulation has been destroyed.

A polyvinylchloride compound filled with 60% glass flake is not able to provide the positive physical spacing accomplished by the glass braid layer. The glass flake, however, enables the polyvinylchloride to survive many of the serve tests to which the previous wire was subjected without destruction of the primary insulation.

The addition of glass flake to silicone rubber for extrusion on wire increases the short term thermal life of the insulation.

"Method and apparatus for producing films and flakes from heat-softenable materials," B.P. 956 832, (Apr. 1964), British Plastics Federation Abstracts, Ser. 19, No. 6, p. 1249, (June 1964).

A method is given for the production of glass flake in the form in which it can be used for reinforcing plastic material, for which purpose it must have high strength properties and uniform thickness. Descriptions and diagrams of the apparatus are given.

(d) Other

Stone, J. T. and Luirette, A. J. (Whittaker Corp.), "Process of mixing glass flakes with a normally liquid resin in frozen commuted form," U.S. 3,151,095, (Sept. 1964).

A resin which is liquid at room temperature, e.g., an epoxy resin, is frozen in spray form to produce a fine powder which is then mixed with glass flakes. On thawing, the glass flakes become uniformly coated with resin.

3. Laminates

Armour Research Foundation of IIT: "Investigation of flake laminate," AD 69 971, (June-Aug. 1955).

The article discusses briefly glass flake laminate flexural and tensile testing and strength.

The question of low tensile strength in glass-flake laminates is discussed. The effect of water absorption on the glass-resin interface is seen as one of the major causes of strength decrease. The function of the resin is also discussed with the spotlight on its function as a volume component i.e., glass:resin ratio and the effect of strength properties.

Faloon, J. E., "Glass bonded mica," Materials in Design Engineering Vol. 51, No. 2, 96-99, (Feb. 1960).

Four grades of glass-bonded mica flakes are discussed with respect to physical properties. Glass mica provides: (1) excellent dimensional stability on exposure to moisture and heat (2) heat resistance high (3) high arc resistance, non-tracking, (4) hardness of glass (5) good molding qualities. In general, mechanical properties depend on molding method.

Glass-mica is fairly expensive in general, the cost mainly being determined by five variables: type of glass; type of mica; ratio of glass to mica; characteristics of inserts required; production volume.

Linden Laboratories: "Investigation of flake laminate," AD 103 534 April-June 1956.

Glass flake laminates have been compared with glass fiber laminates in both physical and economic factors and have been found to have the advantage in each case.

A glass flake paper has been used to make good flake laminates. The thickness of the resin layer between glass surfaces has been related to fracture propagation and to strength in the glass-to-resin joint.

Glass flake laminates have been tested by ASTM methods and have been found to have a flexural strength of 48,600 lb/in^2 , a tensile strength of 18,800 lb/in^2 and moduli of 7.4×10^6 lb/in^2 in flexure and 4.7×10^6 lb/in^2 in tension. A table of physical and economic data are presented. Tensile strength is the only serious drawback of flakes. The most important property is unusually high moduli of elasticity.

Linden Laboratories: "Investigation of flake laminate," AD 120 063 November 1965.

The accomplishments on the objectives set for Linden Laboratories on the flake laminate contract are discussed.

Epoxy-polyamide resins have been used to make glass-flake laminates with high glass concentrations (75-85%), high flexural strength (4.5×10^4 lb/in^2) and high moduli of elasticity (6.7×10^6 lb/in^2).

The development, the test procedure, and the properties of flake laminates are presented.

Olin-Mathieson Chemical Company: "Investigation of glass flake laminate," AD 233 969, Jan. 1960.

Three major methods of producing glass flake laminates have been developed: (1) first consists of 2 alternate methods which are multi-step continuous processes using a plenum chamber for spraying the resin on glass flakes, (2) blending resin in centrifuge, (3) dry blending powdered "B" stag epoxy resin and glass flakes.

Most important physical properties of glass-flakes epoxy have been determined. Flexural modulus and tensile modulus were high; tensile strength, Izod impact and shear strength were low. Water vapor permeability almost zero. A direct relationship of glass flake concentration to flexural strength was shown to exist in the range 60-85 wt. percent glass. Criteria for optimum properties established: (1) minimum thickness of flakes and freedom from flaws, (2) high d/t for glass flake, (3) perfect parallelism, (4) minimum thickness of resin binder, (5) complete resin coating of surface, (6) complete freedom from air bubbles, cracks, voids, etc.

Two practical applications have been suggested by this work: (1) rocket exhaust nozzles and (2) rocket cases.

Owens-Corning Fiberglass Corporation: "Glass/Mica reinforced resin products," Plastic-Rapra Abstracts (620), p. 64, B.P. 971,126, (Jan. 1965).

A hardenable composition comprises a liquid phase of hardenable synthetic resin as specified and dispersed within the liquid phase, a discontinuous solid phase comprising glass flakes and mica particles. Also claims the production of a reinforced resin product by preparing a hardenable composition as claimed, shaping it and then hardening the resin. The preferred resins are polyester, epoxy, and phenolic, but the invention is also applicable to thermoplastics. The glass flakes have a beneficial effect on the dielectric strength of a reinforced resin product.

4. Properties

W. R. Beck and N. W. Taylor, "Glass elements with high-refractive index," U.S. 2,726,161, (Dec. 1955).

This patent discusses transparent glass elements, such as glass beads, fibers, and flakes, and thin plates, having a thickness less than 2 mm and of definite composition. The glass elements have an n of 2.1-2.5. The glass elements have high optical-dispersion values and high dielectric constants. They are chemically stable and stable to sunlight and to exposure to humid atmosphere. The product is adapted for use as sphere-lens optical elements in the manufacture of reflex-reflecting products, such as are used for highway signs and markers.

S. W. Bradstreet, "Principles affecting high strength to density composites with fibers or flakes," AD 603 308 (May 1964).

The high strength of thin metallic and organic fibers, whiskers, and flakes can be exploited if they are properly protected and bonded together by a suitable adhesive or matrix material. The principles which appear to influence the strength of this specimen and their mechanical behavior in such a matrix are reviewed in this report. Qualitative attention is given to series and parallel failure mechanisms in the fibers, to the description of brittle behavior, to bonding and mechanisms of stress transfer, and to testing methods and evaluations. Semi-quantitative relations are adduced to suggest optimization of mechanical properties, and composites containing SiC are discussed to illustrate these relations.

On the basis of principles discussed, suggestions are made for selecting future composite materials and designing them for specific applications.

A. W. Brown, "Plastic compositions containing mixed reinforced materials," Owens-Corning Fiberglass Corp., Belg. 622,995, U.S. 3,158,828 (1962).

This patent deals with sileceous reinforcements both glass flake and glass fiber combined with mica particles so as to achieve structural and dielectric properties as well as to afford a good appearance, while eliminating the defects and the shortcomings of each particular reinforcement by itself. The special properties and effects offered by

each of the three reinforcements are discussed in detail. Processing techniques are discussed along with specific composition of the composite, and a few applications are pointed out. Various resins and coupling agents are also listed. A very informative discussion from an expert in the field of reinforcements.

A. W. Brown, "Glass-flake reinforced epoxy laminates," SPE Journal, Vol. 18, No. 10, p. 1259-1263 (Oct. 1962).

Properties, advantages, and applications of glass-flake laminates are reviewed. The specific laminate discussed is the glass flake reinforced epoxy laminate. Two conjectures are made: first, properties can be improved by increasing percentage of flake in laminates; second, flatter flakes are desirable.

Some of the more important listed properties are:

(1) no blistering nor delamination at 250°C in 50 seconds; reasonable peel strength
(2) outstanding volume and surface resistivity
(3) excellent dielectric strength parallel to laminations at 55 KV due to the fact that there are hundreds of parallel flakes with no one discreet layer
(4) dielectric properties derived from structure of flake laminate itself
(5) promises excellent flexural strength (50,000 psi); dependent on amount of flake
(6) flammibility low (maximum of 2 seconds), low coefficient of expansion
(7) temperature resistance still to be explored but there are satisfactory indications
(8) excellent resistance to internal oxidation and to moisture vapor transmission.

R. Davis, "Non-fibrous filler for RP," Reinforced Plastics, No. 6, p. 8-9, (1963), British Plastics Federation Abstracts, July 1964, p. 1569.

The use of non-fibrous fillers in the production of reinforced plastic materials is considered. The properties of a number of these fillers are compared in tabular form and some properties are discussed in detail.

Included in the table are fillers in the form of flat plates, e.g. aluminum silicates, mica; random irregular shapes, needle-like, and spherical particles. Specific gravity, average size, bulk density, thermal conductivity, coefficient of thermal expansion and heat resistance are listed for metals, inorganic compounds, organics and pigments.

L. Gilman, "Properties of glass-flake reinforced plastics," Monsanto Company, Boston, Mass., AD 233 158, Proc. of Sixth Sagamore Ordnance Materials Research Conference, p. 304-318 (1959).

This report gives an excellent theoretical discussion of the prominent properties of flakes and glass flake laminates.

The properties of flake laminates are accompanied by experimental data on moduli (both flexural and tensile), directional properties, glass percentages, etc.

This is an extremely informative report.

A. L. Leurette, "The properties of compression molded, glass flake reinforced, resin composites," AD 265 885 (1961).

Four molding compositions using glass flake as reinforcement were selected for study by means of a series of tests. The physical, electrical, and mechanical properties of the compositions after compression molding into flat laminates were determined. Simple geometric shapes such as a hemisphere were compression molded from these compositions. The properties of the simple shapes were compared to the properties of the flat laminates.

It was observed that movement of the resin flake mixture in the molds resulted in very poor alignment of the flakes within the molding. This improper alignment resulted in significantly reduced mechanical properties. It was concluded that this problem is inherent to presently available glass flake reinforced molding compounds and will prohibit the satisfactory compression molding of everything but extremely simple shapes such as flat plates using available molding compounds and molding techniques.

Owens-Corning Fiberglas Corp, "Composite structures of glass flakes and transparent synthetic resins," B.P. 832,963 (1960).

Flat glass flakes or platelets, with or without the addition of transparent lubricants, and dispersing, adhering, or coating agents, are incorporated into films of transparent synthetic resins, such as polystyrene, poly(vinyl chloride), poly(vinyl alcohol) or copolymers of vinyl chloride with vinylidene chloride. The products are stronger than unreinforced films in both directions and have a desirable pearly appearance. Glass flakes may also be introduced into foamed synthetic resins to improve strength and heat resistance.

Owens-Corning Fiberglass Corp., "High modulus, high temperature laminates with fibers and flakes," AD 439 692 (1962).

A program to determine the properties of plastic laminates prepared from high melting glass fibers resulted in a retention of 31% of room temperature flexural strength at 1000°F and 22% at 1500°F. The loss in strength was believed to be primarily due to marked thermal decomposition of the resin matrix at the elevated temperature.

A program to determine the properties of plastic laminates prepared from YM-31-A (high modulus) glass flakes resulted in an increase of 25% in compressive strength over laminates prepared from "E" glass flakes. Other properties were comparable.

A program to investigate the properties of a specific type of high temperature fibers for use in reinforcing plastics resulted in their rejection for this use because of low fiber strength. However, forming conditions and equipment used may vary significantly and affect the strength obtained from a particular glass composition. This is particularly evident from the initial data reported herein for X-994 glass, compared to the very high strengths that are presently being obtained.

G. Rugger, "Glass flake laminate," SPE Technical Papers, Vol. III, p. 393-396 (Jan. 1957).

The possibilities of a glass-flake laminate are studied in this article. A list of the major problems encountered are given, such as making the flakes, finding the optimum resin layer thickness, keeping the flakes parallel.

Some of the more important physical properties were discussed; first, equal strength in all directions in the plane of the laminate, high moduli in flexure and tension, possible economic advantages because no weaving would be involved, and resistance to penetration of various forms of energy. Also high percentages of glass can be incorporated by using flakes.

A general investigation of the various possible methods of preparing the flakes were discussed but with no success. The major problems center around getting improved flakes and seeing that the strength of the flake is imparted to the laminate.

The mechanical properties of flakes are compared to those of fiberglass in a table at the end of the article.

H. E. Pelby, Jr., "Plastic composites," Chem. Eng. 71 (1), 75-82 (1964).

Plastic materials, reinforced with filaments, fibers, flakes, or other particles, have been developed for military purposes but are expected to have important applications in the chemical industry.

Glass-flake coating has provided superior corrosion resistance as compared to granular fillers and fibrous reinforcements such as glass mat and glass cloth. The parallel orientation of the flakes also provides good moisture and vapor resistance. But a serious drawback for structural application is low tensile strength (1-2×10^4 psi). There is no data listed to back up his general statements.

M. A. Sadowsky, "Transfer of forces by high strength flakes in a composite material," AD 263 969 (1961).

Isolated microfibers and isolated microflakes do not contribute to strengthening of the composite material. Stress concentrations arising at the ends of isolated microelements will easily reach proportions threatening to destroy the surface bond between microelements and matrix. Whenever this happens the end portions of the microelements become totally inactive. The same kind of inefficiency is inherent in a sequence of microelements aligned along a common line (plane). Such arrangements will not help to build a strong composite material. It was intuitionally recognized, and has now been confirmed by mathematical elasticity analysis, that the basis of strength of the composite lies in the staggered arrangement as shown in illustrations in the report and in force transfer by means of shearing stresses.

L. P. Suffredini, "Stiffer Reinforced Plastics," Materials in Design Engineering, Vol. 54, No. 4, p. 95-97 (1961).

The advantages of glass flake as opposed to fiber structures are listed: (1) greater rigidity and strength due to better packing of more glass, (2) isotropic in strength, (3) low moisture absorption and gas permeability, (4) exceptional dielectric strength, (5) potentially lower cost due to better fabrication techniques.

Included is a discussion of resin evaluation with resin requirements (a) no volatiles formed during cure, (b) low shrinkage during cure, (c) good wetting ability on unfinished glass surfaces. A Narmco epoxy resin called X270 seems to allow for maximum strength. Included is a table comparing two types of flake-reinforced epoxy laminates.

Another table compares electrical properties to those of standard laminates. The flake composites show very good ablation characteristics, e.g. K at 250°F (70% flake by weight) is on order of fiber-reinforced - 1.5 BTU/hr/sq.ft/°F/in. Flake laminates show excellent burning characteristics. Finally, statements on the potential of flakes are given.

B. GLASS TAPES AND RIBBONS

1. Ribbons

G. Laufer, "Dying and reinforcing synthetic resins, G.P. 1,021,161, Chemische Fabrik Billiwarder Aht.-Ges., (1957).

Glass fibers, mats, fabrics, or ribbons which have been dyed in the melt are used for simultaneously dying and reinforcing synthetic resins in which they are embedded. Colored patterns of any kind may be obtained.

2. Tapes

R. A. Humphrey, "Glass microtape," Materials Science Research (by-Otte and Locke), Plenum Press, N.Y. p. 275 (1965).

Progress toward making research specimens of an entirely different filament-wound structure is described. Glass-fiber reinforcement plastics have been shown by others to have mechanical properties superior to most metals at cryogenic temperatures. However, the resin phase is permeable to hydrogen.

The objective of this work is to wind low-permeability shells as suitable containers for cryogenic liquids. The plan is to draw continuous glass microtape about .0005 in. thick by 30 to 50 times wide, and subsequently filament wind the microtape into cylinders.

The preform attenuation method which entails drawing a filament from a preform as it passes slowly downward through a small furnace is used to draw microtape from sheet glass. Only through careful study of the dynamics of the drawing process has a furnace design been developed which produces a flat microtape without an edge bead. A

typical microtape is about 10μ thick and 400μ wide. The winding of microtape into solid, perfectly packed structures has developed into a separate research task. A commercial textile spooler has been modified to provide the fine, uniform transverse necessary for perfect side-by-side placement of microtape into a helically wound, virtually all glass, resin-bound cylinder.

C. GLASS FIBERS OF NON-CIRCULAR CROSS-SECTION

W. J. Eakins and R. A. Humphrey, "Studies of hollow multipartitioned ceramic structures," NASw-672 by DeBell and Richardson Inc. NASA CR-142 (1964).

Results are presented of a fifteen month program of forming glass filaments whose shape is other than a solid round. The feasibility of drawing precise geometric shapes of fibers is demonstrated. With the objective of high stiffness-to-weight ratio, most of the fibers were drawn into hollow cross sections of various shapes for subsequent filament winding. Of particular interest are hollow hexagonal, trigular, and rectangular filaments. Suprisingly complex hollow fibers can also be drawn by the highly refined preform attenuation process used in this program.

A general discussion of production procedure is given. The article does not concentrate on the theory behind the advantages of the different shapes of cross section.

B. W. Rosen, N. F. Dow and Z. Hashin, "Mechanical properties of fibrous composites," General Electric Co., Report, Contract NASw-470, NASA CR-31 (1964).

Very little space is devoted to elliptical fibers in this paper. The experimental study of elliptical fibers is directed along the lines of improving transverse modulus of fibers.

Some questions of interest are "what is the transverse effectiveness of elliptical inclusions of various aspect ratios"? and "how long need the ellipse be to permit substantial load transmission into it by shear from the binder"? Further consideration is directed toward these questions.

No theoretical or experimental conclusions listed at all.

D. KAOLINITE REINFORCEMENT

G. P. Larson, "Kaolinite fractions; their effect on physical properties of reinforced plastics," Mod. Plastics, 35, No. 9, p. 157 (1958).

Kaolinite (china clay) occurs in two shapes, plates and stacks, each fraction having its own physical properties. The physical properties of low, medium, and high unsaturated reinforced polyesters were generally upgraded by addition of the proper kaolinite fraction. The medium unsaturated polyester showed the largest increase. Most of the physical properties of the two types of chlorinated polyesters

tested were improved or unaffected except for tensile strength which was significantly reduced. Every physical property tested was significantly improved by the addition of kaolinite to reinforced diallyl phthalate plastic. The physical properties of the reinforced epoxy resin were generally improved with kaolinite. The phenolic resin maintained the same physical properties except for tensile strength.

Thus, the good effects on the resins used in the evaluation of clay fillers proved very conclusive. The major advantages of kaolinite over other fillers were improved smoothness and gloss, lower peak polymerization temperature and shrinkage, reduced water absorption, and lower material costs.

A large amount of data and graphs are given to substantiate the arguments presented.

F. B. Lotspeich, "Strength and bulk density of compacted mixtures of kaolinite and glass beads," Soil Sci. Soc. Am. Proc. 28, No. 6, p. 737-40 (1964).

Compacted mixtures of kaolinite and glass beads were used to test a hypothesis that the number of contact points of a matrix influences its strength. Four glass bead mixtures were used: (1) a single-sized bead, (2) two sizes of beads designed to permit cubic but not tetrahedral packing, (3) two sizes of beads designed to permit tetrahedral packing of the largest size beads, (4) four sizes of beads designed to permit tetrahedral packing. From 2-40% clay was added to each glass bead mixture; moisture tension at time of compaction from 1/3 to 15 bars.

Conditions of maximum strength and compaction were:

(1) Clay content: this would vary with clay species and particle size distribution of sand fraction. There is an optimum clay content.
(2) A multicomponent sand composed of several size fraction. Maximum strength and compaction occur for tetrahedral packing (4) with mutual contact of all grains with films of clay surrounding all particles.
(3) Moisture between 1-5 bars tension. Less water results in insufficient lubrication and more water will interfere in packing arrangement because of its volume requirements.

E. MICA FLAKES

1. Application

(a) Insulation

F. A. Barr and J. P. McCarthy, "Development of ultra-high temperature dielectric materials for embedding and encapsulating electrical components," Synthetic Mica Corp., ASTIA AD 265 499, (1960-61).

Investigations were conducted on using a phosphate synthetic mica dielectric material for encapsulating and embedding electronic components for 500°C use.

Physical properties of the system were determined and found to be suitable for high temperature use. The major deficiency of the material was in the area of porosity or high water absorption.

Various methods of reducing porosity were investigated including dry pressing, glass coating, additives and various phosphate bonds. The use of a devitrified glass sealing cement as a coating for the phosphate synthetic mica resulted in a composite material cured below 500°C, having good physical properties with water absorption less than 1%.

Several commercial capacitors, transformers and motors were encapsulated and tested. Prototype high temperature resistors were constructed and encapsulated for 500°C applications using cermaplastic injection molding techniques in combination with the phosphate-mica dielectric material.

L. J. Berberick, "Electrical insulating material," U. S. 2,416,143 (1947).

Laminated electrical insulating material having low power factor and non flowing qualities at high temperatures (175°) is prepared from mica flakes and a bonding agent composed of the reaction product of 5-25 parts of maleic acid half ester of castor oil and from 95-75 parts styrene plasticized with an organic compound of substantially zero dipole moment, such as diamylnapthalene.

L. J. Berberick and H. M. Philophy, "Electrical coils insulated with mica and synthetic resins," U.S. 2,656,290 (1953).

The coils are wound with mica tape which is made by binding mica flakes to a pliable sheet backing. The coils are submerged in a completely polymerizable liquid; after impregnation they are removed from the liquid and heated to give a thermosetting resinous coating.

K. L. Berry, "Electrical insulation," Can. 441,543 (1947).

Alternate layers of roughened mica flakes and finely-divided polymerized $CF_2:CF_2$ are bonded under pressure at 330-450° and rapidly cooled. This product is used for electrical insulation.

E. G. Dingman, "Laminated mica - a new insulating material," National Conference on the Application of Electrical Insulation, p. 50 (1960).

This paper discusses in general the properties of mica and mica laminates in relation to electrical insulation. Mica paper is specified. Physical properties, such as high strength and moduli, fire resistant and toughness along with the excellent electrical properties of mica paper make possible uses in new areas, e.g. terminal boards, etc. where both mechanical and electrical properties are required.

Tables are included showing electrical and physical properties of mica-epoxy laminates.

An additional property of mica laminates is its offering of low resin content which gives extra properties such as water impermeability. A discussion follows on shapes of laminates.

E. G. Dingman, "Mica as a reinforcing material for printed circuit and terminal board," SPE Tech. Papers, Vol. VII, Sect. 3-4.

Mica paper may be used as a reinforcing material to make electrical laminates which have electrical and physical properties equal to an epoxy-glass laminate in addition offering stiffness, fire retardancy, retention of properties, a coefficient of expansion close to copper and other properties unique to mica laminates.

F. Eichenauer and E. Eichenauer, "Micaceous insulating material," Ger. 1,126,467 (1962).

An insulator for electrical heating apparatus consists of fine mica flakes with silicone-resin binder. For better distribution of binder over the mica surface, the silicone resin is diluted with C_6H_6; the mica flakes, suspended in water, are stirred into the C_6H_6 solution and well mixed. The mass is then best separated on a centrifuge, pressed or otherwise worked into desired shapes, dried in vacuum and heated to about 300° with further finishing into desired shapes. Such shapes may contain the resistor curves of special heaters.

N. C. Foster and H. M. Philophy (to Westinghouse), "Insulating electrical material with polystyrene-backed mica tape," U. S. 2,917,420 (1959).

A mica tape is bonded to a film of doubly oriented polystyrene on one or both sides. The binder is a resinous polymer, nonvolatile at room temperatures, with a viscosity of 25-10,000 poises at 25°. The tape is then used with a suitable liquid aromatic monomeric compound to produce electrical conductors. The latter is completely impregnated with insulations containing mica flakes and a solid thermosetting resinous compound.

P. S. Hessinger and T. W. Weber, "Development of a synthetic mica ceramic suitable for use at 750°," Am. Ceram. Soc. Bull, 39, 10-13 (1960).

A new process is described in which synthetic mica is precipitated during firing as the primary crystalline phase in a lead glass binder resulting in a ceramoplastic of unusual properties. The material can be machined by ordinary shop tools using techniques analogous to standard glass-bonded mica fabrication. This factor plus low dielectric loss, and a thermal coefficient of expansion matching stainless steel has resulted in successful preparation of sealed terminals and headers fired-on printed circuits and other special electronic insulation components.

M. D. Heyman (to Integrated Mica Corp.), "Phosphate-impregnated integrated mica sheets," U. S. 2,865,426 (1958).

A material is described which is strong, substantially nonhygroscopic, capable of withstanding temperatures up to 2000°F, good dielectric properties, can be made in thicknesses as little as 0.002 in. and capable of being stamped or die cut. The process consists of integrating

mica flakes (either natural or synthetic) into porous sheets in which there is a multiplicity of pores, impregnating the sheet with a silicone resin, drying and gradually heating the sheet up to 1000°F to drive off organic material and leave a shell of SiO_2, reimpregnating the sheet with a dilute ortho-phosphoric acid solution and a volatile solvent, heat-treating to 500-600°F and pressure of 100 lb/sq.in. and finally reheating to 1700°F to eliminate the water of crystallization of the flakes.

R. J. Ketterer, "Mica paper insulations - state of the art" Insulation, Vol. 10, No. 9, p. 24-32 (1964).

Mica is useful as an insulator because of its desirable electrical mechanical and thermal properties. Mica paper is a flexible material in a continuous and highly uniform sheet, which eliminates the stiffness and irregularity of conventional mica products. Mica paper also possesses much of the durability and resistance to destructive forces because of its overlapping structure.

Mica paper possesses excellent thermal resistance and excellent electrical properties.

A long discussion of mica paper forms and applications is included as well as various manufacturing processes.

D. W. Lewis and H. M. Philophy (West. Elec. Corp.), "Electrical conductors insulated with thermosetting polysiloxane resins," U. S. 3,069,302.

The conductors are prepared by applying to an electrical conductor a composite insulation consisting of mica flakes joined with viscous liquid polysiloxane binders. The conductor and applied composite insulation are impregnated with a completely polymerizable fluid polysiloxane composition. This assures complete filling of all the pores of insulation.

P. Nowah and F. J. Bollig, "Mica laminates containing silicone resins," Patent-Verwaltungs - G. m. b. H., Ger. 1,035,824 (1958).

A mixture of silicone resins is used to bond and laminate mica for insulation purposes. The resin consists of polysiloxanes with a R:S ratio (R = alkyl or akyl) < 1.9:1 in combination with low-mol. Si resins containing 0.1-0.3% of active H atoms and catalysts and hardening agents. The resins provide adhesives for mica which dry out after heating at 140-180° for 15 minutes, but which at higher temperatures flow and fill the air spaces between the conductor and the insulating laminate.

C. D. Richardson and A. F. Zarist, "Treated mica paper insulation," U. S. 2,707,204 (1955).

Backed flakes of mica, mica paper or mica tape are coated and impregnated with a mixture of an acidic glyceryl polyester resin and a complex epoxide resin to provide mica insulation for electrical machine windings, such as armature windings for use in turbine generators. A detailed discussion is given for the type of polyester resin under consideration.

P. Robinson and D. Pech, "Dielectric materials," U. S. 2,704,105 (1955).

Improved dielectric materials are formed by alternately laminating layers of mica or glass suspended in a F-containing poly(tetrahaloethylene) binder with a softening point above 200°. The mica or glass particles have a maximum thickness of 0.2 mil and a maximum linear planar dimension of 10 mils.

D. A. Rogers, Jr. and R. J. Hillen (Westinghouse Elec. Corp.), "Composite mica insulation," U. S. 3,026,222 (1962).

This invention relates to composite mica insulation, and in particular, to flexible insulating materials embodying mica and a specific resinous binder. This invention relates to electrical conductors insulated with the composite mica insulation. The mica flakes are applied to a pliable sheet along with a resinous binder composition to form a strong and flexible insulating material.

The binder comprises 10-90% of a mixture of unsaturated polyesters and 10-90% of a liquid unsaturated monomer capable of vinyl-type polymerization. The binder is used to wet mica flakes which are then deposited on a single backing or as a filler between two sheets as the insulation.

W. Schick, "Electric capacitors," U. S. 2,745,048 (1956).

Assembled electric capacitors comprising metal electrodes, mica plates between the electrodes, supporting insulator plates, and connecting wires or strips, are embedded in plastic materials to give protection against moisture and mechanical damage. Increased water resistance is imparted to the assembled capacitors if they are coated with a mixture (4:1) of mineral powder and an oil-modified aklyd resin before being embedded in plastic.

E. L. Schulman and J. S. Johnson, "Electrical insulation," U. S. 2,479,417 (1949).

A composite insulation composed of mica flakes and a sheet backing of glass fiber or asbestos cloth, with a resinous binder, is applied to conductors and heat-treated so that only decomposition products of the resinous binder remain, then the whole is impregnated with a solventless insulating resin. Such a resin eliminates undesirable voids that would occur as a result of evaporation and trapping of solvent. Copper ordinarily inhibits polymerization of solventless viny-type resins.

E. L. Schulman, "Mica insulating composition," U. S. 2,495,186 (1950).

Electrical appliance insulating compositions of exceptional strength and freedom from tackiness during cure are prepared from mica flakes and 2-4% of a binder composed of shellac 65-90, castor oil 5-20, and a fine-wood resin insoluble in a petroleum hydrocarbon 5-15%.

G. R. Shepherd, "Insulating material," B.P. 568,071, (1945).

Mica-flake sheets and similar forms of mica are bonded by a resinous material, such as polymerized isobutylene having an average molecular weight of 3000-20,000. The insulating laminated material thus produced resists hardening with age.

F. Schwartz, "Impregnated mica paper is excellent insulator," Materials in Design Engineering, Vol. 52, No. 1, p. 114-116 (1960).

Mica paper with synthetic resin impregnants provides a family of excellent insulating materials with a variety of characteristics. There are two large classes of materials (a) resin-impregnated plate (b) combination materials.

Epoxy and silicone resins are the most widely used resins for the first class. For maximum strength, reinforcements are added to mica, e.g. glass cloth, Mylar polyester film. Various types of grades are listed for the combination class.

The properties available from mica paper are high dielectric strength, excellent dimensional stability, heat resistance, but tensile strength is not very high.

W. R. Watson, Jr. and J. Suiss, "Flexible mica insulation," U.S. 2,562,004 (1951).

A bonding material for loose mica pieces, yielding improved flexibility, is composed of 95-50% of liquid α-methylstyrene polymer, molecular weight 300-4000 and 5-50% copolymer of 50-90 parts monostyrene and 50-10 parts of at least 1 unsaturated aliphatic hydrocarbon, such as butadiene, isoprene, and isobutylene, molecular weight 2000-30,000. Other resins may be used. The binder content is 3-15% of weight of mica flakes. The product resists a temperature of 150°. Breakdown strength per mil in 30 mil thickness is 1000-2800 v.

"Electrical insulating composition," Fr. 857,481 (1940).

Mica fragments are impregnated with a polyvinyl acetal and molded. Solvents may be used for the impregnation. Condensation resins may be added. The product is used as an electrical insulating composition.

A. G. Werke fuer Elecktro-Isolation und Wichlerei Einrichtungen, "Micafil" Electrically Insulating Foils, Belg. 611,715 (1962).

Electrical insulating foils of high thermal stability consist of a combination of a mica foil with a layer of an elastomer based on vulcanizable silicones. The silicone elastomer is coated on the mica base in the form of a solution, e.g. xylene, and the solvent is evaporated by heating.

(b) Corrosion

J. G. Ford and A. J. Kuti, "Westinghouse reports high durability for mica-based paint system," Paint, Oil and Chem. Rev., 113, No. 26, p. 12-27 (1950).

This article describes a paint system in which there are three coats, the second containing a "shingle roof" effect of mica flakes. The mica wards off moisture, water vapor, and corrosive substances. In addition, mica increases heat stability of the coating as much as ten times at elevated temperatures.

M. D. Heyman, "Applying protective coatings of mica to solid surfaces," U. S. 2,568,004 (1951).

The cleaned surface of material to be protected, such as metal, may first be coated with a thin layer of plastic material, and while this is still soft layers of small "nascent" mica splittings suspended in a small amount of volatile liquid, such as H_2O, MeOH, xylene, or toluene, are sprayed or brushed on to give a layer at least 2 mils thick, with pauses for evaporation, until the desired thickness is obtained. Or the step of plastic coating may be omitted. When dry the surface is covered with a thin lacquer coating to fill the interstices among the flakes. The product contains 95-98% of mica.

G. J. Raymond, "Corrosion protection," Fr. 988,039 (1951).

The metal surface to be protected is covered with a layer of bituminous paint and then an intimate mixture of graphite and mica flakes and of glass powder is applied by means of a spray gun to give a decorative and anticorrosive finishing layer on the metal.

(c) Optical

E. F. Klenke, Jr. and A. J. Stratton (E. I. duPont de Nemours), "Flaked, micaceous pigments," Belg. 619,446 (1962).

A translucent, micaceous substrate is coated with a thin, translucent C layer obtained by pyrolysis of aliphatic hydrocarbons. The pigments may contain an intermediate translucent layer of TiO_2 and ZrO_2, which is deposited by hydrolysis followed by calcination, before deposition of the C layer. These pigments produce an iridescent effect due to optical interference.

(d) Other

W. Schneider and A. W. Worthington (to Westinghouse), "Flexible, resin-bonded mica articles" U. S. 2,772,696 (1956).

Flexible insulating members, e.g. tubes, channels, flat sheets, or angles, having excellent physical and dielectric properties are prepared from mica flakes and partly cured, thermosetting-resin binders. A list of criteria for determining a suitable resin binder is given. A production technique for the various shapes is given.

2. Fabrication

(a) Synthetic Mica

General Services Administration (D.C.): "The synthetic mica research program," AD 290 250.

This program contained nine contracts: (1) synthesis of new types of mica, (2) research on delamination, sheet-making, and bonding for use in capacitors and electron tubes, (3) surface chemistry of mica flakes and infiltration of mineralizers within layers, (4) edge-bonding of flakes, (5) delamination, reconstitution and heat-pressing of synthetic mica to produce substitutes for natural mica in capacitors etc., (6) reconstitution by electrophoresis of mica sheet, (7) delamination studies, (8) fine-grinding and recrystallization, and (9) studies of certain basic properties of synthetic mica, e.g. rebonding of split laminae, and effects of ultra high pressure and temperature on rebonding.

The major results were (1) development of paper suitable for capacitors, and (2) sheets satisfactory for tube spacers.

R. A. Hatch, (to Minnesota Mining and Manufacturing Co.), "Synthetic mica flakes and sheet material therefrom," U. S. 3,001,571 (1961).

A general method is described for obtaining flexible sheet material of synthetic F-containing mica of high tensile strength. This invention provides a mica sheet with improved mechanical properties and with no binders necessary. Blended mixtures of mica platelets and various fibers and flakes yield new properties. The mica flakes produced have extremely large surface areas yet they are very thin.

3. Properties

E. G. Dingman, "Epoxy-mica paper laminate reinforcement," SPE Journal, Vol. 17, No. 9, p. 981-983 (1961).

Mica paper can be used to make laminates having electrical and physical properties equal to those of epoxy-glass laminates. Potential cost of mica reinforcement is about one-third that of fiberglass.

In the article there are extensive tables of the mechanical and electrical properties of both types of mica paper [i.e. integrated (phlogopite) and reconstituted (muscovite)]. Briefly, mica laminates offer stiffness, fire retardency, low coefficient of expansion, low moisture absorption, and excellent electrical properties.

Mica papers are of two principal types: reconstituted mica and integrated mica, the former receiving a thermal treatment during processing resulting in some alteration, the latter composed of basically unaltered mica. The laminates were prepared with epoxy resins. Two types of papers were used -- integrated mica paper based on phlogopite and reconstituted mica based on muscovite. The latter possesses superior properties but the former has a few peculiar properties.

F. METAL FLAKES

1. Application

(a) Optical

H. C. Felsher and W. J. Hanan, "Gold-bronze pigments for aerosol paints," Paint and Varnish Prod. (1963).

Bronze pigments consist of flat, highly polished flakes of pure copper or copper-zinc alloy (e.g. Palegold - 11% Zn, Richgold - 30% Zn). There is some flake surface oxidation. For bright specular reflection, smaller size flake and parallel orientation is required. A method of treatment of stearic acid coating acts to bring flakes undamaged to the surface in nearly parallel orientation. There are other methods described when leafing is not desired. The above pigments also possess tarnish-resistancy.

The article concludes with a discussion of aerosol spray considerations and special bronze color effects possible.

H. C. Felsher and W. J. Hanan, "Brilliance for plastics through metallics," Modern Plastics, p. 96 (1963).

This article is mainly devoted to gold and copper bronzes, comprising completely opaque flakes of copper-zinc alloys and nearly pure copper respectively. They reflect light of the red and yellow wave length range predominantly.

Brilliance is a function of flake orientation and surface condition and size. A complete description of modifications of metallic color is included for unique esthetic possibilities. The major problem encountered - orientation of metallic flakes - is discussed in great detail. Other harmful influences due to processing, e.g. high temperature, are discussed.

H. C. Felsher and W. J. Hanan, "Reflective metallic flakes in ablative plastics," SPI Proceedings, 20th Annual Conf., p 17-E (1965).

This article discusses the feasibility of improving the performance of ablative materials by incorporating a metallic flake material which reflects radiant heat. The possible advantages of reflection as a means of eliminating flux, over re-radiation and pure boundary-layer ablation are analyzed. A theoretical discussion of ablation and thermal heat flow are included.

The various available reflective materials are described and evaluated as to their possible value. Recommendations are made regarding possible methods of incorporating reflective flakes within the framework of structural requirements and present production methods.

H. C. Felsher and W. J. Hanan, "Evaluation and description of metallic colours," SPE Journal, Vol. 11, Sec. 9-4, (1965).

This article contains a broad discussion of metallic flake reflectors in a matrix. Metallic flakes have high reflectivity and complete opacity, and pearlescent flakes possess transparency. The types of metals discussed are Al, Cu, and Al-alloys (brasses). Al possesses high reflectance throughout visible spectrum, Cu and Cu-alloy in red or long-ware region. Graphs are included comparing spectral reflectance of various coatings.

The major portion of the article is devoted to a deep and thorough discussion of variables involved, such as orientation of flakes, and a discussion of the various decorative effects which can be obtained by different combinations or arrangements of the flakes available. Some of the more important problems are also discussed.

Finally, the article discusses the future instrumentation possibilities and present methods of evaluation.

S. Yolles (to E. I. duPont de Nemours), "Reflective pigments," U. S. 3,053,683, (1962).

This patent describes a method of making shiny metal-coated glass flake pigment which is weather resistant. The method comprises decomposing in a closed vessel a gaseous thermally-decomposable organometallic compound in the presence of smooth discrete glass flakes having a particle size of 50-400 mesh, whereby a bright coating of metal is deposited on the flakes. The metal is of the class containing chromium, aluminum, molybdenum, and nickel. The flake used is not necessarily limited to glass as examples are given in which mica flakes and aluminum flakes were used, etc.

(b) Conductor

V. I. Shorokhora, "Features of electric conductivity of plastics from polystyrene and nickel flake," Plasticheshie Massy, No. 3, p. 23-5 (1965).

This paper discusses the use of fillers in polystyrene to render electrical conductivity. An introduction of powder fillers shows that a large amount of powder is needed to transfer charge. By introducing flake fillers into the polystyrene by means of copper-nickel decomposition after which the copper was disssolved gave the results that much less nickel flake is needed to give a given decrease in resistivity of polystyrene than powder filler. The mechanical properties of the flake were also shown to be better in various tests. Graphs are shown comparing the resistivity of the flake versus powder under varying concentrations.

Also included was a discussion on the influence of the flake form on the properties of flake. It was shown that a square flake is somewhat inferior to a rectangular shape in electrical resistivity properties, water absorption.

2. Fabrication

H. B. Whitehurst, "Investigation of metal-glass composite materials," AD 112 796 (1955).

This report discusses progress on the problem of combining glass with metal by three basic methods, (1) consolidation of metal coated glass fibers or flakes by pressure applied at elevated temperatures, (2) direct mixing of glass fibers of flakes with molten metal, and (3) formation of glass fibers or films within a metallic matrix by hot working metal bars containing finely divided glass particles. The discussion is largely directed towards the practical and theoretical limits of the tensile strength imparted by the reinforcements.

The discussion is almost exclusively limited to fibers, but it is stated that the discussion would be similar for flake glass reinforcement.

3. Properties

(a) Aluminum Powders

E. Gregory and N. J. Grant, "Aluminum powder products composed," Iron Age, Vol. 170, p. 69 (1952).

Aluminum products made from three grades of sintered aluminum powder were tested in creep-rupture at temperatures from 400° to 900°F for times up to 1000 hr. Included were a coarse atomized grade, M-255, and two types of flake powder with different oxide contents, M-257 and SAP. Materials made from the flake products show unusually good high temperature stability. Extreme gains in rupture life and creep resistance are achieved by use of the powdered aluminum products as compared with conventional forged and cast aluminum alloys.

A variety of tables and graphs are listed for the given properties of the powdered products mentioned above. No theoretical discussion is included, but a good deal of data is listed.

E. Gregory and N. J. Grant, "High temperature strength of wrought aluminum powder products," AIME Trans. Vol. 200, p. 247-254 (1954).

The creep-rupture properties of wrought aluminum powder products made from fire grades of sintered aluminum powder were investigated at temperatures from 400-900°F for rupture times up to 1000 hours. The effect of stress concentrations on materials of this type were investigated by means of notched creep rupture tests. A tentative correlation was obtained between the creep-rupture properties and the structure as resealed by electron micrographs.

A variety of diagrams, graphs, and data are listed in the article and a reasonable amount of theory is developed.

F. V. Lenel, A. B. Bachensto and M. V. Rose, "Aluminum powder metallurgy," PB-121136, p. 85 (1955).

The procedures used at RPI in producing aluminum powder extrusions from flake aluminum pigments powders and from atomized powders are described. From tests of powder properties and mechanical properties of the extrusions, it was found that the yield strength at room temperature and at 400°C increased directly with the square root of the reciprocal of the average flake thickness and that the weight percent of oxide was not as important as the flake thickness in strengthening these extrusions. The properties of these extrusions have also been compared with the properties of extrusions which were produced by other companies.

F. V. Lenel, G. S. Ansell and E. C. Nelson, "Metallography of aluminum powder extrusions," Trans. AIME, 209, p. 117 (1957).

This article discusses the discovery that extrusions of fine aluminum flake powders posses remarkable high-temperature strengths and discusses the production of a new class of engineering materials whose properties are desired from a fine dispersion of oxide particles in a metallic matrix.

The paper focuses on a metallographic investigation of experimental and commercial sintered aluminum-powder extrusions, and hence goes into a detailed discussion of microstructure.

F. V. Lenel, A. B. Bachensto and M. V. Rose, "Properties of aluminum powders and extrusions produced from them," Trans. AIME, 209, p. 124 (1957).

This article discusses the effect on tensile and yield strength of aluminum powder extrusions of powder particle size or flake powder thickness. Oxide content is shown to have very minor effects so the degree of oxide dispersion was found to have major effects.

A number of tables and graphs are shown to support the general theories about the mechanical properties listed.

G. GENERAL

"The promise of composites," Materials in Design Engineering, No. 210, p. 79-126 (1963).

An extremely comprehensive review of the field, giving a good introductory perspective of composites, the general nature of a composite materials, plus a discussion of laminar, particulate, fibrous, flake, and filled composites. Included are the various types of composites in each of the above five divisions.

The four page section on flakes is very comprehensive and includes a discussion on all facets of the flake field.

This report is one of the best available in the open literature.

A. M. Shibley, Plastec Report 1, "State of the art: flake-glass laminates," AD 244 104, p. 1-121 (1960).

Achievements in the production of glass flake and glass-flake laminates are presented in this report. Covering the period 1953-1960, the report summarizes results under three main headings:

Section 3 Manufacture and Testing of Glass Flake
Section 4 Coating Glass Flake with Resin Binders
Section 5 Flake-Glass Laminates: Properties and Fabrication

Experimentation with and production of glass-flake laminates began in this period. Much preliminary thinking and experimentation went into the effort to produce the first samples. Some first starts were not carried to completion because more fruitful ways of making the laminates were presented. However, it is yet too early in the game to write off as a total loss some of these earlier efforts. That is why this report summarizes progress from the beginning to the final production of glass-flake laminates. It is expected that such information may be valuable for current, as well as for contemplated future, activities in the field.

V. APPENDIX

LITERATURE COVERED IN THE SEARCH

Advanced Chemical Engineering	1960 - present
AIChE Journal	1958 - present
Am. Chem. Soc. Div. Org. Coatings and Plastics Chem.	1961 - present
Am. Chem. Soc. Div. Polymer Chem. Papers	1960 - present
Battelle Technical Review	1960 - present
British Chemical Engineering	1961 - present
British Plastics	1960 - present
Canadian Journal of Chemical Engineering	1960 - present
Canadian Journal of Technology	1954 - 1957
Chemical Abstracts	1946 - present
Chemical Engineering	1960 - present
Engineering Index	1955 - present
Industrial Engineering Chemistry	1956 - present
Industrial Engineering Chemistry Fundamentals	1962 - present
Industrial Engineering Chemistry Process Design and Development	1962 - present
Industrial Engineering Chemistry Product Research and Development	1962 - present
Index American Doctoral Dissertations	1955 - present
Index Theses/Gr. Britian and Ireland	1955 - present
Japan Journal of Applied Physics	1962 - present
J. Appl. Chem. U. S. S. R.	1955 - present
J. Appl. Polymer Science	1959 - present
J. Chem. Engineering Data	1959 - present
J. Polymer Science	1955 - 1962
J. Polymer Sci. Pt. A, Gen. Papers	1963 - present
J. Polymer Sci. Pt. B, Polymer Letters	1963 - present
Materials Design Engineering	1960 - present
Materials Res. and Standards	1961 - present
Missiles and Rockets	1963 - present
Modern Plastics	1955 - present
Nature	1960 - present
Physics and Chem. Solids	1960 - present
Plastics Design and Process	1963 - present
Plastics Inst. London, J. and Transactions	1961 - present
Proceed. Acad. Sci. USSR Sect. Chem. Tech.	1960 - present
RCA Revue	1961 - present
Record Chem. Progress Kresge-Hooke Science Lib.	1960 - present
Reinforced Plastics	1963 - present
Rept. Progress Polymer Physics Japan	1961 - present
Resins and Rubbers Plastics	1955-59, 1962

SAE Journal	1958 - present
SAE Trans.	1958 - present
Soviet Phys. Tech. Phys.	1961 - present
Soviet Plastics/Eng. Trans.	1962 - present
SPE Journal	1962 - present
SPE Tech. Papers	1955 - present
SPE Trans.	1961 - present
SPI Journal	1955 - present
Polymer Science USSR	1960 - 1964
British Plastics Federation Abstracts	1961 - present
International Aerospace Abstracts	1965
Technical Abstracts Bulletin	1960 - present
Scientific and Technical Aerospace Repts.	1963 - present

VI. ACKNOWLEDGMENTS

I wish to thank Dr. Lawrence E. Nielsen for his expert technical guidance throughout this project.

I wish to thank Dr. Tom L. Tolbert for his interest in this project and his critical review of the final report.

I am also very grateful to Mrs. Charlotte M. Bower for her constant assistance in both the bibliographic and technical aspects of this project.

bjn
3/9/66

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Monsanto Company	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

TAPES AND RIBBONS IN COMPOSITES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Literature Survey

5. AUTHOR(S) (Last name, first name, initial)

Charlotte M. Bower

Richard A. Landy

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
August 31, 1965	48	122

8a. CONTRACT OR GRANT NO. N00014-66-C-0045	9a. ORIGINATOR'S REPORT NUMBER(S) HPC 65-5
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. XXXXXXXXXXXXXXXXXX Distribution Statement:
Each transmittal of this document outside the Department of Defense must have prior approval of the Director, Material Sciences Division, Office of Naval Research

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13 ABSTRACT

Two-dimensional microstructures, e.g., flakes, plates, tapes and ribbons, offer unique properties as reinforcements for composite materials. There is little reported work in this area. The majority of the references are to glass, mica, and metal flakes which have been examined for electrical uses. Fabrication methods for glass flakes have received the most emphasis from industry. A few papers dealing with tapes and ribbons are cited.

DD FORM 1 JAN 64 1473 0101-807-6800

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
composites	2	3	8	3		
reinforcements	8	3	9	3		
flakes	1	2				
plates	1	2				
tapes	1	2				
ribbons	1	2				
literature survey	0	0				
metal	0	0				
glass	0	0				
mica	0	0				

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (*TS*), (*S*), (*C*), or (*U*).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.